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CONTENTS

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ERRATA IN TRANSACTIONS OF THE OPTICAL SOCIETY,
33, 49, 50 (1931–32).

*Rapid Spectrophotometry with Bi-Multiple Spectra and a
New Type of Wedge Cell.*

Equation (14), p. 49, should read:
$$\log_{10}(t_2/t_1) = -\,da + \log x.$$

Equation (16), p. 50, should read:
$$a = \frac{\log_{10}(t_1/t_2) - (0{\cdot}3 + 2{\cdot}0L)}{d}.$$

535·243

A NEW APPARATUS FOR RAPID SPEC-TROPHOTOMETRY OF LIQUIDS IN THE ULTRA-VIOLET REGION

By F. TWYMAN, F.R.S.

ABSTRACT. The paper describes an instrument for the rapid spectrophotometry of liquids by the spectrographic method. A single exposure, usually of less than 20 seconds, results in a set of spectra which embodies all that is necessary for plotting an absorption curve.

§ 1. INTRODUCTION

ABSORPTION spectrophotometry as now carried out is tedious, and a way of hastening the process would be of advantage if only to save time; but when the substance under examination is unstable, and particularly when it is altered by the irradiation which is essential for the measurement, the results may be valueless if the duration of the irradiation is sufficient to cause material change.

This paper describes an instrument by means of which the data for determining the complete absorption curve of a substance can usually be obtained with an exposure of 20 seconds or less.

The device originated from a suggestion made on September 5, 1931, by L. J. Spencer, one of the staff of the laboratory of Adam Hilger, Ltd. A number of embodiments of the principle used have already been fully described*, but the one to be described in the present paper is new.

§ 2. PRINCIPLE OF THE APPARATUS

An essential part of the apparatus is a cell with a wedge-shaped recess which contains the absorbing liquid. Wedge cells have been used before to yield in a single photograph a qualitative survey of the absorption spectrum of a liquid. When quantitative results in the ultra-violet are desired the principle first used by V. Henri is generally employed, usually in the form designed by the present author†. The arrangement is well known, but will be recapitulated to make clear what follows.

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* *Trans. Opt. Soc.* **33**, 37 (1932).   † *Phys. Rev.* **8**, 674–88 (1916).

Two beams of light proceeding from the same source are fed into the spectrograph, one beam having passed first through a fixed aperture, the other through a variable aperture which we will suppose to be formed by the usual rotating sector. By varying the size of the latter aperture the relative intensities of the beams, and hence the effective density* of the system, can be varied within wide limits. In the path of the beam which passes through the fixed aperture is placed the substance under test, which in general absorbs the radiation in varying proportions at different parts of the spectrum. By means of a suitable optical system spectra formed by the two beams are brought close together and photographed, and it is in general found that at one or more points in the pair of spectrograms the intensities are equal. For those wave-lengths, the density of the column of liquid is equal to the effective density of the sector.

Further pairs of spectrograms are then obtained with different sector apertures, and the data thus accumulated for a complete (density, wave-length) curve. If the thickness of the absorbing substance be known, this curve may be converted into one of (extinction-coefficients, wave-lengths)†. The number of pairs of spectrograms needed depends upon the amount of detail required in the curve, a common number being about fifteen.

As described in the paper cited, a combination of a wedge cell and a multiple-aperture slit diaphragm enables the fifteen or more spectrograms to be obtained simultaneously. The use of a wedge cell transfers the variation in density from the comparison beam to the beam which passes through the absorbing liquid. The use of two multiple-aperture diaphragms yields fifteen or more pairs of spectra, each pair resulting from one beam which has passed through a certain thickness of liquid and a second beam from the same source which has passed through a known density.

§ 3. THE NOTCHED WEDGE CELL SPECTROPHOTOMETER

The simplest arrangement was briefly mentioned in the paper already referred to. In this the absorbing liquid is contained in a wedge-shaped cell such that
a, t, h $\quad t = ah$, t being the thickness and h the height from the bottom of the cell. The cell being placed in front of the slit of a spectrograph, a photograph is taken through one set of apertures placed close to the slit; a second photograph is then taken through the same cell, now containing the solvent only, another set of apertures being used whose positions are intermediate between those of the first set.

In a development of this scheme the two sets of photographs are obtained simultaneously, two cells being used, one containing the absorbing and the other the comparison liquid.

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* "Density" is used in the sense defined by Hurter & Driffield, *J. Soc. Chem. Ind.* **9**, 455 (1890) i.e. density $(D) = \log_{10}(I_0/I)$, I_0 being the intensity of incident radiation and I that of the transmitted radiation. For the sense in which the rotating sector can be said to have a density as thus defined, see page 18.

† Extinction coefficient $\epsilon = D/t$, t being in cm. Sometimes not distinguished in the literature from the molecular extinction coefficient (or, as it is sometimes called, the molecular absorption coefficient) which $= \epsilon/C$, C being the concentration of the substance in gram-molecules per litre.

The method employing two cells is the one preferred, and in this the arrange-ment of parts is as in figure 1. The light from a single source passes through a condenser of quartz to the two cells. The two cells drop easily into recesses, and the whole mount is attached to the slit of the spectrograph.

The condenser is fixed on the cell mounting, and on the latter is engraved the correct distance of the light-source to ensure that all rays which pass through the slit pass through the lenses and prism of the spectrograph and eventually reach the photographic plate.
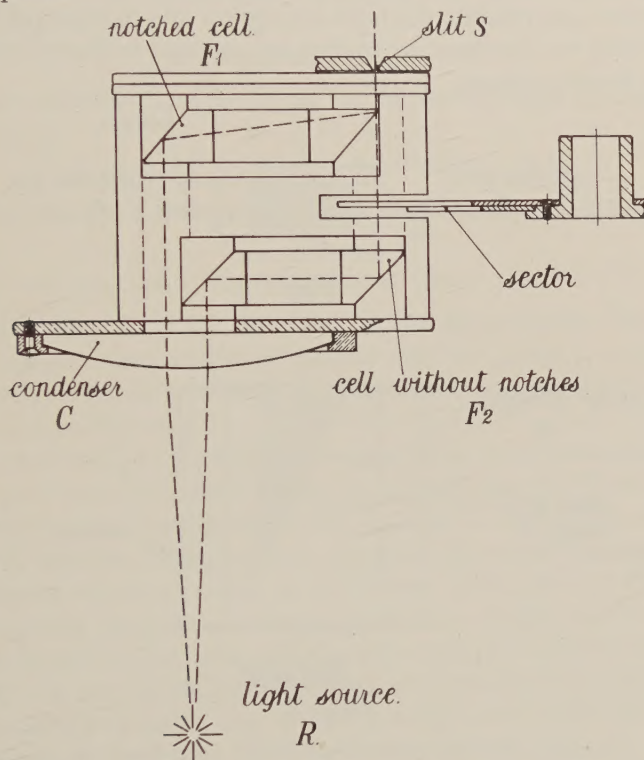
Figure 1.

The cells are made of fused silica. One cell, shown in figure 2, contains the absorbing liquid in a wedge-shaped recess W, so that the radiation reflected at face F_1 traverses different thicknesses of liquid at different heights. The reflecting faces F_1 and F_2 are parallel, and so inclined that the ray falling on the middle of F_1 is reflected to the edge of F_2, so that the side of the cell does not interfere with the operative pencils of rays. After passage through the wedge of liquid the rays are reflected on the second reflecting face F_2, except where that face has been interrupted by a series of notches ground in its edge.

The second cell is exactly like the first, except that it has no notches in the edge, and that the rays which fall on the middle of F_1 are reflected to the middle of F_2. This latter cell contains the liquid with which the absorption of the first liquid is to

be compared; usually one whose absorption is assumed to be negligible (water or alcohol, for instance), or, if the liquid under test is a solution, the solvent used for that solution. The radiation transmitted by the second cell passes between the notches in the first cell. In the path of this second beam can be placed one of two devices of which one, a rotating sector, is indicated in figure 1. Others will be described later. The function of the sector or other device is to reduce the intensity of the beam in a known way.

The spectrograph, whose slit is placed at S, then yields a series of spectra of which every other one exhibits the local absorption due to different thicknesses of the solution, while the intermediate spectra are reduced uniformly throughout the spectrum by a known amount.
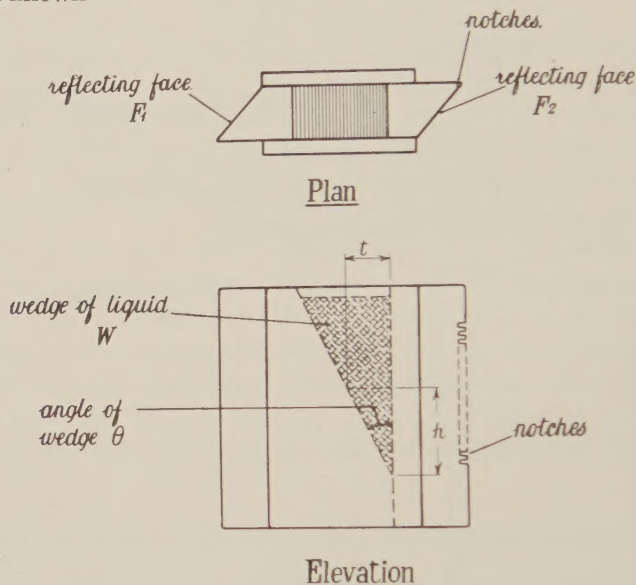
Figure 2.

At certain wave-lengths the spectrum which is subject to absorption by the liquid will equal in intensity the neighbouring one and for these wave-lengths one can therefore easily deduce the "density" of the thickness of absorbing liquid through which the rays have passed.

Several forms of wedge cell have been investigated, and before describing the one finally adopted it will be desirable to pass under review the other forms and the reasons for their rejection. They are attractive at first sight, and their disadvantages not very obvious except after some consideration.

§ 4. THE VARIOUS TYPES OF CELL

θ

In the first two-cell arrangement made the angle θ of the wedge of liquid was $\tan^{-1}\frac{1}{2}$; thus, on the assumption that all the rays passed horizontally through the cell, the length t path of the rays through the liquid was $\frac{1}{2}h$, h being the height of the horizontal ray above the bottom of the wedge.

The notches, of which there were 25, were each 0·367 mm. wide, and separated by 0·367 mm.* The bottom of the bottom notch, which corresponded with the top dividing line between spectra, was 2 mm. above the apex of the wedge of liquid, and therefore the rays which emerged there had passed through 1 mm. of liquid. The rays which emerged from the top of the top notch (which corresponded with the bottom dividing line between spectra) had passed through 1·0 cm. of liquid. Thus the thickness in cm., t, of liquid traversed by the ray which emerged from the nth notch edge from the bottom (corresponding with the nth from the top in the spectrogram) is given by:

n

$$t = 0·1 + 0·01836\,(n - 1) \qquad \ldots\ldots(1).$$

The extinction coefficient, ϵ, of the liquid for the match points of adjacent spectra is therefore given by:

ϵ

$$\epsilon = D/t = D/\{0·1 + 0·01836\,(n - 1)\} \qquad \ldots\ldots(2),$$

where D is the density of the rotating sector or other comparison density.

D

§ 5. ERRORS OF THE NOTCHED-WEDGE CELL OF CONSTANT ANGLE

The error (arising from the necessity of matching visually the photographed lines) in any single measurement of density may be $\pm$ 0·02†, so that where the density measured is below 1 an error of 2 per cent or more may arise in the extinction coefficient from this cause.

In the notched-wedge cell of constant angle, since in our estimation of match we proceed by equal steps, i.e. since Δh and Δt do not vary with h or t, the density-increment given by each step is $\epsilon\Delta t$ or $D\Delta t/t$, since $\epsilon = D/t$. In the wedge cell now described Δt is constant, hence a single step from the match point gives a variable density-increment which is greatest at the bottom of the cell and least at the top.

Taking an actual instance let us suppose that $D = 0·398$, and $\theta = \tan^{-1}\frac{1}{2}$. Then the density increment at the bottom of the cell, where, at a match point, $\epsilon = 3·98$, is $3·98 \times 0·0184 = 0·073$. At the top of the cell, where at a match point $\epsilon = 0·398$, the density increment for a single step is 0·0073, which is not detectable. Thus there are more steps at the top of the cell than are of any use.

A cognate drawback to which this type of cell is subject is that the ϵ-values obtained are not uniformly spaced. The number of values for a given range of ϵ diminishes as ϵ increases, hence it generally happens that the regions of greatest interest (usually around the peaks of the absorption curves) have fewest points, whilst the less interesting regions (the valleys between the peaks) have a much

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* It is not pretended that it is possible to make the notches and gaps so precisely to size as is here suggested, but it is possible to ensure that in the making of the notches no cumulative error occurs, so that the edges of each notch are in the positions complying with the expression given below to an accuracy of 0·05 mm. It is desirable that the positions of these edges should be checked on a micrometer.

† F. Weigert, *Optische Methoden in der Chemie*, p. 237 (Leipzig, 1927). The figure is one which finds fairly general acceptance as of the highest accuracy attainable under favourable conditions. von Halban and Eisenbrand (*Proc. R. S.* A **116**, 154) in quoting Weigert say that an error of 0·04 in D is normally to be expected.

greater number of ϵ-values available. This is illustrated in figure 3, which shows the extinction coefficient of potassium nitrate as obtained with the first trial cell.
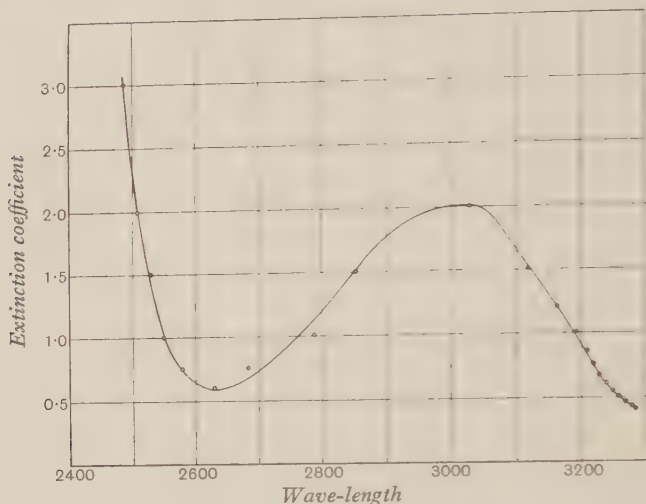
Figure 3. Absorption curve of potassium nitrate.

These drawbacks are due to the fact that the angle of the cell is constant. They may be overcome in the following manner:

§ 6. CELL GIVING EXTINCTION COEFFICIENTS UNIFORMLY SPACED

A form of cell which will give extinction coefficients uniformly spaced has one interior face in the shape of a rectangular hyperbola. To give a thickness of liquid ranging from 0·1 cm. at the bottom of the cell to 1·0 cm. at a point 1·8 cm. from the bottom requires the side of the cell to be of such shape that $t = 0.2\,(2.0 - h)$. Such a curve, whilst giving extinction coefficients uniformly spaced, suffers from the objection that the variation in the density of the liquid for a single step from the edge where, for a given wave-length, the match takes place, to the next higher one, is many times smaller at the bottom than at the top of the cell. This may be shown as follows:

Given a fixed comparison density D; when an extinction coefficient ϵ is being measured at height h, a change of Δh (i.e. one step) produces a change ΔD in D given by $\epsilon = D/t$ and $\epsilon = (D + \Delta D)/(t + \Delta t)$.

Substituting for t,

$$\epsilon = D\,(2.0 - h)/0.2 = (D + \Delta D)\,\{2.0 - (h + \Delta h)\}/0.2,$$

whence
$$D\Delta h = \Delta D\,(2 - h).$$

But
$$2 - h = 0.2/t = 0.2\,\epsilon/D,$$

whence
$$\Delta D = D^2 . \Delta h/0.2\epsilon.$$

Now Δh and D are constants in this expression, hence as ϵ increases the change in D (i.e. ΔD) produced by moving one step from the match point diminishes, so that again some of the steps in density may be too small to detect, while elsewhere they are a number of times greater than the least that can be detected.

§ 7. CELL GIVING UNIFORM DENSITY INCREMENTS

We next consider a form in which the steps vary in magnitude so as to give uniform density-increments from the edge where a match is made to the next edge.

Let D be the comparison density (fixed).

Let ϵ_h be the extinction coefficient at height h (thickness t). The condition to be fulfilled is that

$$\epsilon_h \frac{dt}{dh} = K.$$

Now
$$\epsilon_h = D/t,$$
$$\therefore\ D.dt/t = K\,dh.$$

On integration,
$$D \int_{t_0}^{t} \frac{dt}{t} = K \int_{h_0}^{h} dh,$$

or
$$D \log_e (t/t_0) = K\,\{h - h_0\}.$$

Suppose that
$$t_0 = 0\cdot 1 \quad \text{when} \quad h_0 = 0$$

and
$$t = 1\cdot 0 \quad \text{when} \quad h = 1\cdot 8,$$

then
$$D \log_e (1/0\cdot 1) = 1\cdot 8\ K,$$
$$\therefore\ K = 1\cdot 279D.$$

Hence
$$\log_e 10^t = 1\cdot 279h,$$

or
$$e^{1\cdot 279h} = 10t,$$

or
$$t = 0\cdot 1 e^{1\cdot 279h}.$$

The adoption of this form of cell was therefore considered. It is shown in figure 4. The making of such a cell presents no insuperable difficulty. I have had occasion to devise a machine for polishing non-spherical lenses which can be adapted for this purpose, and seems likely to give a sufficient accuracy. Unfortunately, however, the deviation due to refraction between the fused silica and the liquid (which is present to some extent in all the types so far discussed) can become very large in the top portion of such a cell.

The error thus introduced may be treated first on the assumption that we are dealing with an actual point source, and an example will illustrate the magnitude of the effect.

In the case of the cell whose equation is $t = 0\cdot 1 e^{1\cdot 279h}$ the error will be variable owing to the varying slope, but it will be a maximum at the top of the cell.

$$t = 0\cdot 1 e^{1\cdot 279h},$$
$$\therefore\ dt/dh = 0\cdot 1279 e^{1\cdot 279h}.$$

Put h equal to 1·8.

Then $dt/dh = 1·279$, whence $\theta = 52°$.

Taking water as the liquid, at wave-length 6563 ($\mu = 1·4564$ for fused silica, 1·3311 for water)

we get
$$\sin r = \frac{1·4564}{1·33115} \times \sin 52° = \frac{1·4564}{1·33115} \times ·809,$$

whence
$$r = 62° \ 18',$$

and the deviation is 10° 18'.

The path traversed is thus $t/\cos 10° \ 18'$, which $= t\ 0·984 = 1·016t$ approximately. Thus, if the user of the cell makes the assumption that the rays pass through the liquid horizontally, he may be in error by any amount up to 1·6 per cent depending upon the height in the cell at which he is working. With water, this error will change very little throughout the spectrum.

One further example is of interest. Methyl iodide has a refractive index of 1·737 for wave-length 5890, while that of fused silica is 1·458.

noteh edge.
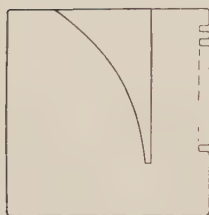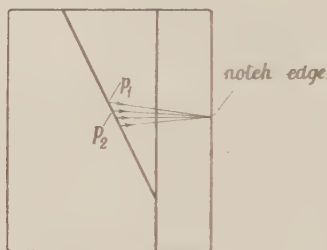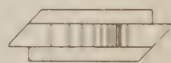
Figure 4.

Figure 5.

Figure 6.

Here, at the top of the cell, we have

$$\sin r = \frac{1·737}{1·458} \times ·809,$$

or
$$r = 74° \ 27',$$

whence the deviation is 22° 27'.

Therefore the light path $= t/\cos 22° \ 27' = t\ 0·9242 = 1·075t$ approximately or the path would be increased by 7·5 per cent.

It will be observed that the error in t can be quite large.

A more serious objection arises in that with deviations up to 22° it is certain that in many cases light passing through the top part of the cell would not reach the photographic plate at all. The examples quoted are sufficient to illustrate the magnitude of the effect, and to show that it may be serious.

It has been assumed, in order to simplify the calculation, that the light source is a point source. This, however, is not the case in practice, and in general the light source will be of finite dimensions. The effect of this is to produce a spread of the beam so that the pencil of light passing through a point adjacent to a notch edge is

not homogeneous as regards its length of path through the liquid. This effect has been calculated for the simplest case—the cell of constant angle, where $\theta = \tan^{-1}\frac{1}{2}$.

I have made the calculation on the assumption that the light-source is uniform throughout a height of 3 mm., the intensity of illumination at a notch edge being found by integrating the elementary pencils $p_1, p_2, \ldots$ (see figure 5) which converge upon that edge, each subjected to the absorption of the appropriate thickness of liquid traversed. Taking a refractive index $1 \cdot 5$ for both liquid and cell, the liquid having an extinction coefficient of 2, I find that if the match is made at the bottom of the cell ($t = 1$ mm.) the effective intensity of illumination of the point A is about 1 per cent greater, and if the match is made at the top of the cell about 1 per cent less, than if the light source were concentrated into a point. Whilst the calculation has been performed for the simple wedge cell, it is obvious that for the curved cells the effect will be much larger at the top of the cells owing to the larger angles involved.

The effect has not been analysed for liquids whose refractive index differs from that of the cell, but it would appear that the effect would be diminished when liquids of higher refractive index than silica were being examined, and vice versa for lower refractive index liquids.

There is still one other error and this is due to the device employed to obtain the two photographs simultaneously. The beam is not parallel to the sides of the cell but makes a mean angle therewith of 7°. Since the cosine of 7° is 0·9925, an error of less than 1 per cent is caused by this in the measurement of the path-length. The error in the extinction coefficient will be in the same proportion. If desired this can be allowed for by multiplying the extinction coefficient as measured by 0·9925, though the error is less than is observable by visual examination of the photographs.

It will be realized that when, as in all the forms of cell described above, the light does not enter the cell at normal incidence, then a complex of errors arises, such as those described above, owing to refraction and dispersion. The only sound way of dealing with these is to have normal incidence, and a stepped or echelon cell is adopted to secure this*.

§ 8. THE ECHELON CELL

The form of cell finally adopted will now be described. In this the principle has been retained that each thickness of liquid should bear a constant ratio (actually 1·292) to the thickness of the liquid next below it. The result of this is to make the changes in density for one step from the match point the same regardless of the height. This means also that if, as is preferred by some workers, the values of $\log_{10}\epsilon$ are plotted as ordinates, these values are equally spaced vertically on the absorption curve. Incidentally it may be remarked that since D is constant for one set of photographs the ϵ's are all known to the same percentage accuracy. The complete cell is shown in figure 6. It is to be understood that two cells are used, mounted

* The idea of a stepped cell is not new. B. A. Winter Blyth used a stepped cell for the measurement of absorption coefficients, but merely to obtain a number of fixed lengths of liquid. A photograph was taken through one step and then the cell was racked up and a photograph taken through the next step, and so on. *J. Chem. Soc.* **75**, 1162 to 1166 (1899).

as described in connection with figure 1, the only difference between them being that one is notched and the other not.

It will be seen that the external shape of the cell is that of a rhomb, and the recess in which the liquid is placed has been formed by building up a number of strips of fused silica of diminishing length. The fused silica pieces of which the cell as a whole is built are joined together without cement by the process described by Parker & Dalladay*. As has already been described, along one edge of the rhomb are ground notches through which a comparison beam can be transmitted whilst the beam passing through the cell is reflected from the surfaces remaining between the notches.

t_0 There are ten thicknesses of liquid, of which the bottom one may be designated t_0 (cm.). The cell has five notches. Each notch is 1·8 mm. wide, and the pitch of the notches is 3·6 mm. The steps in the cell are each 1·8 mm. high, and the edges of the steps are opposite the mid-point of a notch and of a projection alternately. Since the second (comparison) cell is exactly like the first, the bottom notch edge separates the beam which has passed through t_0 cm. of absorbing liquid from a comparison beam which has passed through t_0 cm. of the comparison liquid. The next notch edge separates a pair of beams which have passed through $t_0 \times$ 1·292 cm. of absorbing and comparison liquids respectively, and so on. More generally, if n be the number

n of the notch edge counting 0, 1, 2, etc. from the bottom, the nth edge will separate beams of the two liquids both of which have passed through the same thickness of liquid

$$t = t_0 \times 1 \cdot 292^n.$$

Thus there are ten pairs of spectra.

Two types of cell have been provided, one varying in liquid-thickness from 0·1 to 1 cm., the other, for very absorptive liquids, from 0·01 to 0·1 cm.

$\Delta\epsilon$ If we are dealing with a comparison density D, and are measuring an extinction coefficient ϵ, the change $\Delta\epsilon$ corresponding to one step is found by writing

$$\epsilon = D/(t_0 \times 1 \cdot 292^n),$$
$$\epsilon + \Delta\epsilon = D/(t_0 \times 1 \cdot 292^{n+1}) = \epsilon/1 \cdot 292,$$

whence $\Delta\epsilon = 0 \cdot 226\epsilon.$

If values of $\log_{10}\epsilon$ are plotted, such values are uniformly spaced.

Suppose we wish to know the difference in density corresponding to one step from the match point.

$$D = \epsilon t_0 \times 1 \cdot 292^n,$$

and $D + \Delta D = \epsilon t_0 \times 1 \cdot 292^{n+1} = 1 \cdot 292D,$

$$\therefore \; \Delta D = 0 \cdot 292D.$$

In order that it may be possible to use them for measuring the absorption of 1 cm. of liquid without filling them to the brim, the cells are made amply high, and can thus be easily put in their mounting or removed without spilling. Thus, very little care suffices to ensure that the outsides of the cells are kept from getting wet.

* *Trans. Far. Soc.* **12**, 1 (1916).

§ 9. USE OF THE NOTCHED-WEDGE ECHELON CELL

The apparatus being in position in front of the slit, the light-source must be put in the right position. To this end both the cells are filled with liquid by means of a pipette, care being taken to keep them clean and dry on the outside. The cells are placed in their recesses in the cell mount, the light-source is set at the correct distance from the condenser (as marked on the mount), and the spark is started. The spark should be set on the axis of the condensing lens (see figure 1) as nearly as is possible by inspection. Using a wide slit, the observer, on looking in at the right-hand side of the camera end of the spectrograph towards the prism of the spectrograph, will then see the light-source imaged within the aperture of that prism. The light-source should be moved until its image is central with the prism aperture. The observer can then be sure that the radiation which reaches the spectrum along the two alternative paths (through the absorbing and comparison liquids respectively) is not reduced in intensity by vignetting.

The slit width having been reduced to 0·03 mm., a spectrogram may be taken to make sure that all the spectra match throughout their whole length. If they do not, some want of adjustment is indicated.

The cells are then removed, cleaned, filled (one with the absorbing liquid and the other with the comparison liquid), and replaced in their recesses. The sector should then be started, a few seconds being allowed for it to get up speed. The dark slide with its plate is put in the camera, the shutter opened, the spark started, and an exposure given. The plate having been developed, fixed, washed and dried, the observations can be made immediately.

The reduction of the observations can be made in a very simple manner as follows. A table is prepared showing the length of path through the liquid for every notch edge n. It having been observed that for a certain wave-length a match is observed for the nth notch edge, the path corresponding to this notch is obtained from the table and divided into the known comparison density D. The resulting figure is the extinction coefficient for this particular wave-length.

It is anticipated that this device will frequently be used with quartz spectrographs which incorporate a wave-length scale. On these instruments the wave-length scale is normally adjusted to suit a much narrower width of spectrum than is used in the notched cell here described. Thus the wave-length scale will be impressed on the spectrum itself, and may obscure match points in a number of spectra. The points which become in this way difficult to read can be repeated by taking a second photograph with a fresh comparison density; as, for instance, a fresh setting of the sector.

Reading the plate and recording the observations. The only difficulty in reading the plate arises from the great amount of information which is compressed into small space. For this reason a simple arrangement has been devised whereby the observer can see at a glance, whatever part of the spectrum he is examining, the number of each spectrum strip as measured from the top of the plate (which corresponds with the bottom of the cell).

F. Twyman

A photographic reference plate is prepared on which numbers are photo-graphed, in black on a clear ground, corresponding with each spectrum. To prevent scratching of the negative a rubber band is put round each end of the reference plate, which is then laid on the negative, the latter being supported in a viewing stand illuminated from below. Looking at the negative with an ordinary watchmaker's glass, the observer adjusts the reference plate until the numbers come just above the proper dividing lines which separate the spectra: he is then able, without any undue strain on his attention, to examine the photograph for the match points, and to record the wave-length of the match points and their numerical designations.

Selection of comparison density, and ranges of extinction coefficients measurable. Examination of a number of papers dealing with a variety of liquids shows that the observers used liquids of such strength as to give extinction coefficients of which typical examples are given in table 1.

Table 1.

Reference	Substance	Maximum extinction coefficient
Proc. R. S. B, **106**, 292 (1930)	Normal serum globulin	1·2
Proc. R. S. B, **106**, 1 (1930)	Diphtheria antitoxin floccules	1·2
Biochem. J. **22**, 1499 (1928)	Uric acid	1·46
J. Am. Chem. Soc. **48**, 2202 (1926)	Asymmetric dyes	3·60
J. Am. Chem. Soc. **46**, 581 (1924)	Various indicators	3·60
Ind. & Eng. Chem. **18**, 627 (1926)	Agalma black	3·60
J. Phys. Chem. **30**, 56 (1926)	Simple azo-dye	1·80
J. Am. Chem. Soc. **48**, 1984 (1926)	Benzene azo-benzene	1·5
J. Chem. Soc. **1**, 202 (1930)	Diphenyl derivatives	0·02 to 0·36
J. Phys. Chem. **32**, 751 (1928)	Silver halide emulsions	(0·1 to 2·6 0·02 to 0·55)
J. Chem. Soc. 1421, Pt. 2 (1929)	Sulphur chlorides	40
J. Am. Chem. Soc. **50**, 525 (1928)	Phycoerythrin	0·1 to 1·3
Proc. R. S. B, **104**, 561 (1926)	Ergosterol	1 to 35
	Vitamin D	180
Phil. Mag. (vii) **5**, 944 (1928)	Vitamin A	50 to 100

Since the usable thickness of liquid ranges from 1 cm. down to 0·1 cm. (or with the alternative cell from 0·01 to 0·1 cm.), extinction coefficients in the ratio of 1 to 10 can be measured with any given comparison density.

Supposing nothing whatever is known of the absorption of the liquid to be measured, one photograph should be taken with the maximum opening of the sector, and another with the minimum opening. Selection of a suitable aperture should then be easy.

The regions of chief chemical interest in absorption spectra often lie near the peaks of absorption. If the observer finds that within the whole range provided by the apparatus he fails to get the peaks of the absorptions on his curve, he must dilute the liquid, or if that be not permissible, use a greater density in the com-parison beam. If, on the other hand, he desires to extend the measurements to lower densities, he must reduce the density in the comparison beam, or add parallel-

ended cells between the condenser and the light-source, adjusting the position of the light source so that the correct condition of illumination is maintained.

The sector openings (two in number) can be adjusted so that the total opening* is from 0·4 to 0·7 of a complete circle, enabling densities from 0·155 to 0·398 to be measured. The sector is engraved to read log m, where $1/m$ is the fraction of a revolution to which the sector opening is adjusted. It is mounted to rotate at about 3000 r.p.m. on the shaft of a motor, this being mounted on a separate stand, to avoid communication of vibration to the slit. The sector is so protected that it can be set in position without any risk of its striking the cell mount while in motion.

m

A second sector has also been made in which m is variable from 1·95 to 14·45, corresponding to a range of D from 0·29 to 1·60. With the two alternative sectors and the two cells four arrangements are possible, covering different ranges of extinction coefficient, as follows:

(1) Sector giving a density from 0·155 to 0·398, used with a wedge cell of thicknesses 0·1 to 1·0 cm. This combination gives ranges as follows: (*a*) 0·155 density permits measurements of extinction coefficient to be made from 0·155 to 1·555. (*b*) 0·398 density permits measurements of extinction coefficient to be made from 0·398 to 3·98.

(2) Sector giving a density from 0·29 to 1·6, used with a wedge cell of thicknesses 0·1 to 1·0 cm. This combination gives ranges as follows: (*a*) 0·29 density permits measurements of extinction coefficient to be made from 0·29 to 2·9. (*b*) 1·6 density permits measurements of extinction coefficient to be made from 1·6 to 16.

(3) Sector giving a density from 0·155 to 0·398, used with a wedge cell of thicknesses from 0·01 to 0·1 cm. This combination gives ranges as follows: (*a*) 0·155 density permits measurements of extinction coefficient to be made from 1·55 to 15·5. (*b*) 0·398 density permits measurements of extinction coefficient to be made from 3·98 to 39·8.

(4) Sector giving a density from 0·29 to 1·6, used with a wedge cell of thicknesses from 0·01 to 0·1 cm. This combination gives ranges as follows: (*a*) 0·29 density permits measurements of extinction coefficient to be made from 2·9 to 29. (*b*) 1·6 density permits measurements of extinction coefficient to be made from 16·0 to 160.

Certain ranges of extinction coefficients can be measured in two or more ways. For instance, if $\epsilon = 3$, it could be measured thus:

$$D = 0\cdot3, \ t = 0\cdot3/3 = 0\cdot1,$$
$$D = 0\cdot6, \ t = 0\cdot6/3 = 0\cdot2,$$
$$D = 1\cdot2, \ t = 1\cdot2/3 = 0\cdot4,$$

and so on.

* Hereinafter referred to as the "sector opening."

If the highest accuracy in the determination of ϵ is desired it must be remembered that the measurement of a density by visual comparison of photographs, under such conditions as those under consideration, cannot be made with an accuracy better than about 0·02 in the density, and the accuracy in determination of the density remains of the same absolute value no matter what the value of the density may be*. It is desirable therefore to make the comparison density as high as possible. This has the advantage also that t is large (for any given ϵ), so that inaccuracies in the construction of the cell will be of less importance. The sector must of course be made with an accuracy commensurate with its density.

Examination of the extinction coefficients quoted earlier will show that the range given by the instrument is sufficient for practically all needs.

Alternative comparison densities. An objection to the sector is that there is no simple means of ensuring that the exposure corresponds with a whole number of complete half-revolutions. If less than 50 revolutions occur in the course of an exposure, therefore, with the sector running at 175 r.p.m. (giving 350 complete cycles of exposure), and for shorter exposures than 10 seconds, an appreciable error may be introduced. It is for this reason that the sector is run at high speed.

Various alternatives to the sector for providing the comparison density have been considered. One is a silica plate cathodically coated with platinum, the deposit being rendered durable by being burnt in. Another device might be several plates of very thin glass variously transmissive to the ultra-violet, such as borosilicate crown, u.v. flint, and u.v. crown. Again, a parallel-sided cell containing a solution of known absorption through the spectrum might be used.

As has already been indicated, an arrangement that seems likely to be satisfactory consists of a pile of quartz plates. The maximum number of plates suggested is 12. The density of this pile of plates can be calculated. It has been considered by Stokes† and, more recently, by Smith‡. The formula given by Stokes is

$$\psi(m) = \frac{1-p}{1-(2m-1)\,p},$$

where $\psi(m)$ is the intensity through m plates when the incident intensity is taken as unity and p is the fraction reflected at a single surface. p is obtained from Fresnel's equation $p = \{(\mu-1)/(\mu+1)\}^2$, where μ is the refractive index for light of the wave-length under consideration and p is the fraction reflected at a single surface of the radiation of that wave-length incident upon it. It is assumed that there is no absorption§.

Since μ varies with the wave-length it follows that the density of the pile of

* F. Weigert, *loc. cit.*

† *Proc. R. S.* **11**, 545 (1860–2).

‡ *Trans. Opt. Soc.* **27**, 317 (1925–6).

§ Little is known about the absorption of quartz except that for the short wave-lengths for which it is transmissive, say from 2000 to 1850 A., different specimens and even different parts of the same specimen may differ very greatly in absorption. Owing to this uncertainty the density of the pile of plates should be checked by using in the cell a liquid of known absorption.

plates does so also. The density has been calculated for plates of crystalline quartz cut perpendicular to the axis. From Stokes's formula for wave-length 2062 it is found that the density of a single plate is 0·051, that for six plates is 0·243, and that for twelve plates 0·396. It is customary, when two "densities" are placed in series in a beam, to assume that the resultant density is to be obtained by adding the two separate densities. It will be seen that such an assumption is incorrect where the separate densities introduce separate reflecting surfaces, and may be seriously incorrect where the substance of which the densities are made has but little absorption. The plates of the pile must be kept very clean to avoid scatter of the radiation, and for the same reason care must be taken to see that the polish is very good; a condition not always sufficiently assured by casual visual examination. They must also be of fairly good optical quality, or the correct conditions of illumination may be interfered with. The twelve plates mentioned is a reasonable number to use as a working maximum.

It will be noticed that the sector has the great advantage that it passes the same fraction of radiation for all wave-lengths.

§ 10. CHOICE OF A LIGHT-SOURCE

No matter what type of cell is employed, the choice of the light-source is one that requires consideration. Investigators who have studied and used absorption spectra have sought a light-source which should be as continuous as possible, and the under-water aluminium spark, and more recently special forms of hydrogen vacuum tubes, have been coming into use.

It will be found on examining the conditions of illumination necessary for reliable absorption spectrophotometry that there is the implicit assumption that the source should be a point source, and that its aspects from the directions followed by the two beams to be compared should be identical. The first of these conditions cannot be fulfilled by a hydrogen end-on vacuum tube of the kind in question: while the second can only be assured, even partially, by careful lining up. This danger must be borne in mind and provided for by the usual precaution of taking comparison spectra with the same liquid, e.g. water, in both cells to see that the spectra match perfectly throughout their length.

On these and other grounds I retain a preference for the spark. It is true that occasionally it is difficult to take a reading on the photograph at an interesting part of the absorption curve owing to the weakness of the lines at that point, but provision can easily be made to meet this by taking photographs with several slightly differing comparison densities so that fresh match points can be found in neighbouring positions where there are suitable lines: or, alternatively, extra photographs can be taken with considerably heavier exposure.

Taking photographs with different exposures is valuable from another point of view. In under-exposed and over-exposed parts of a photographic plate the variation of blackening of the plate with the exposure is smaller than in the intermediate regions. The ideal plate and method of development for accuracy would appear to

be those which yield a big gamma. This has the effect of decreasing the latitude of the plate, and necessitates several exposures if the match points are to lie on spectrum lines neither over- nor under-exposed. Owing to the speed with which photographs can be taken with the apparatus now described, it is easy to obtain with a total exposure of one half-minute data which might, according to earlier methods, require exposures totalling more than half an hour. Thus the time for taking the additional exposures is not serious.

§ 11. ALTERNATIVE METHODS OF USING THE WEDGE CELL

In the paper referred to on page 1 is described a method of using the wedge cell whereby the variation of the comparison density is introduced not, as has so far been assumed, by means of a sector or pile of plates, but by one of two other methods. In both of these the two sets of spectrograms are obtained by making two separate exposures. In one method the two exposures are made of the same duration, but the intensity is varied by having the source at two different distances. In this manner no assumptions at all regarding the law of blackening of the photographic plate are introduced, and hence this source of uncertainty is eliminated. In the other method the source is maintained at the same distance throughout, but the time of exposure is varied. This, however, involves uncertainty due to failure of the reciprocity law, and is to be avoided. Both of these methods were abandoned in favour of that whereby the two exposures were obtained simultaneously. Another method comprises the simultaneous use of two different sparks in series at different distances from the slit, one to illuminate each cell. It has much to recommend it, provided one can assure the two sparks remaining always of equal intensity. It is worth investigation*.

§ 12. CONSIDERATIONS CONCERNING THE USE OF A ROTATING SECTOR

In all the methods described in detail in this paper a rotating sector is assumed to be employed, for among devices which are free from colour there is none so suitable. Polarization methods of reducing intensity require the utmost care in design and use if errors, whose existence is not easily to be detected, are to be avoided. Further, polarization methods, dependent as they are on the use of Iceland Spar, cannot be carried beyond about 2200 Å. on account of the failure of transparency of that material.

A wire grid, which in some applications is very useful, is not admissible here since if the spacing of the wires were close enough to be appropriate for the small area presented by the pencil of rays, the manufacture would be very difficult and the diffraction too great to be permissible.

It has been assumed in this paper that the interposition of a rotating sector in which the duration of exposure is $1/m$ of a revolution produces to a close approxima-

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* The work of Barratt seems to show that this can be relied on if two similar sparks are run in series.

tion the same effect on the blackening of a photographic plate as does the same intensity of illumination reduced in the proportion $1/m$ and acting continuously.

Investigations on the blackening of photographic plates have revealed two effects which arouse doubts as to the justice of this assumption, first, the effect of intermittent illumination, secondly, the failure of the Bunsen-Roscoe reciprocity law. It has long been known that a photographic exposure given in instalments does not produce on development the same blackening as if a continuous exposure had been given of the same duration and intensity. The most complete investigation of this effect seems to have been carried out by Raymond Davis, whose conclusion is that the difference varies with the emulsion, the illumination, the number of interruptions, and the duration of the interruptions*.

The failure of the reciprocity law has been most thoroughly studied by Jones and collaborators in a series of investigations, the results of which are given in five papers. In these the conclusion is arrived at that the departure varies with the intensity of illumination, the development, and the kind of plates used†. It is not surprising, therefore, that hesitation has been experienced, and particularly by some of those most familiar with the subject of the photographic process, in using a rotating sector, in which both causes of error are present, for photographic photometry.

It is true that when I introduced the rotating sector for ultra-violet spectrophotometry it was checked with satisfactory results against a wire grid and a polarization photometer, but the results were never published, nor was the investigation exhaustive. From 1914 to 1917 the question has been studied by numerous workers‡, and it is now generally accepted that for intermittencies above 120 per minute and within the limits of accuracy that may be expected in visual photographic photometry, viz. about 0·02 in a measurement of density, the law of reciprocity holds good. Two observations must be made concerning the above statement. First, the sector photometer, with which many of the observations were concerned, has a sector in each of the beams compared, the one sector fixed, the other variable; though in the investigation of Brian O'Brien only one sector was used. Secondly, whenever an oscillating spark is used, the illumination is intermittent in a double sense independently of the intermissions caused by the sectors; for not only are the oscillations of the spark present (tens or hundreds of thousands of oscillations per second), but each train of sparks in all probability dies away before a fresh one commences, resulting in, say, 50 such separate trains of sparks per second.

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* *Sci. Papers Bur. Standards*, **21**, 95 (1926–27).

† *J. Opt. Soc. Am.* **7**, 1079; **11**, 319; **12**, 321; **13**, 443; **14**, 223 (1923 to 1927).

‡ For summary see Twyman and Simeon, *Trans. Opt. Soc.* **31**, 169 (1930). A paper by H. von Halban and J. Eisenbrand (*Proc. R. S.* A, **116**, 153) is also especially pertinent when considered together with the work of Baly, Morton and Riding (*Proc. R. S.* A, **113**, 709); both photo-electric and revolving sectors were employed in the determination of extinction coefficients, and the two methods gave concordant results to within the experimental accuracy of the methods. Recently, investigations by Brian O'Brien recorded in *Phys. Rev.* **33**, 640 (1929), and **37**, 471 (1931), confirmed, for 3600 and 1680 intermissions per minute, the compensation of the reciprocity-law failure by the intermittency effect.

2

Taking into consideration the great complexity of the phenomena present in the use of photographic spectrophotometry I would urge, in spite of the growing consensus of opinion in favour of the rotating sector, that any series of measurements should commence by measurements of the absorption of an agreed common liquid as for instance KNO_3*. This is already done by some workers.

Finally, I should like to repeat the suggestion of the trial, in place of the single light-source and rotating sector, of two similar sparks at different distances, each with its appropriate condenser.

The sectors described in this paper are engraved to read values of log m (see above). If in the use of the wedge cells as here described, at a point of match, the intensity of illumination for the match point is reduced by absorption of the liquid from I_0 to I†, the density D of the liquid $= \log (I_0 I)$. If the reciprocity law holds, $D = \log m$, and it is in this sense that log m is referred to as the "density" of the sector.

§ 13. FINAL NOTE

Since the preparation of this paper one by Oram E. Miller ‡ has come to my notice in which bi-multiple spectra are combined with a wedge effect to give a result somewhat similar to those described in this paper, although fewer strips are obtainable. The methods described here have the advantage among others that they can be applied to existing spectrographs without any modification of the latter. Those interested in comparing the two different methods of approach to this problem should consult the original papers.

A paper by Brian O'Brien has also appeared, in abstract§, in which it appears that bi-multiple spectra are used for spectro-photometry in a way closely similar to that described here, but the wedge effect is produced by a spiral sector, as was also suggested in *Trans. Opt. Soc.* **33**, 37 (1932).

DISCUSSION

Mr T. SMITH said that the term "extinction coefficient" was not a happy one. Why not say "absorption coefficient"?

Dr L. C. MARTIN. The author makes a neat point regarding the time-discontinuity of the spark source, from which he infers that the use of a sector in one beam but not in the other is not of significance as regards "reciprocity". No doubt the same would apply to the hydrogen tube used to give a continuous spectrum. I should be interested to know whether this apparatus can be used with a hydrogen tube without meeting any unforeseen difficulty; no obvious difficulty is apparent.

* See von Halban and Eisenbrand *loc. cit.*

† I_0 and I being expressed in terms of the intensity of radiation of like wave-length transmitted through a like thickness of the comparison liquid which may itself be absorptive. This is the sense in which the symbols are used throughout this paper, a like meaning being implicit in the use of the word density.

‡ *Rev. Sci. Inst.* New series, **3**, 30 (1932).

§ *Bull. Am. Phys. Soc.* **7**, 1 (1932).

We have at the Imperial College tried the expedient of using a coarse-line grating, producing a definitely known range of intensity in the successive maxima, to give an exposure-density scale on the plate. The grating is placed behind the focussing lens of the spectrograph with the lines perpendicular to the slit. This method is quite capable of being developed for accurate work, but would require an auxiliary densitometer, whereas the author's method is self-contained. It may, however, be worth while to continue the experiments.

AUTHOR'S reply. I prefer the term "extinction coefficient" because it has been generally accepted by chemists since its definition by Bunsen and Roscoe, and this cannot be said of any other of the terms used in connexion with absorption of light.

As regards the time-discontinuity of the spark source, I did not mean it to be inferred that I considered this in itself to justify the use of a sector in one beam but not in the other. On the contrary, I rather wished to accentuate the complexity of the phenomenon and the desirability of different observers checking their different methods by the examination of a common liquid, as indicated in the succeeding paragraph of my paper.

The continuous-spectrum hydrogen tube is growing in favour. I think, however, that it requires special care in use for two reasons. First, in using a continuous spectrum it is essential to use an instrument of considerable dispersion, or the erroneous supposition as to the density for a given wave-length, due to error of wave-length setting, may be greater than the direct error of measurement of the density. This is particularly important on the steep flanks of an absorption curve, which regions are often of great importance in the spectrophotometric analysis of mixtures. Now, where a spark source is used, giving a line source, one is in no doubt as to the wave-length, since it is precisely identified by the individual line. Secondly, it is tacitly assumed in the construction of most spectrophotometers that the light originates from a point source, or at least from a localized source all in one plane perpendicular to the optical axis. Such a condition is not fulfilled by an end-on hydrogen vacuum tube, and unless great care is taken to maintain perfect alignment one may, on theoretical grounds, expect a want of balance in the two beams passing through the photometer owing to the different aspects from which, through the two paths, the light source is viewed. Even with the best possible centring, unequal distribution of the source of illumination within the capillary may conceivably be a source of error.

With regard to the coarse-line grating I have used this as a means of reducing intensity, the grating being made by soldering thin copper wire into the grooves of two parallel fine-threaded screws. The device is an excellent one, although I found great difficulty in keeping the wires taut. This however is quite different from the use described by Dr L. C. Martin, on which I do not feel competent to express an opinion.

AN EXPERIMENTAL STUDY OF ELECTRICAL DISCHARGE IN GASES AT NORMAL TEMPERATURES AND PRESSURES

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ABSTRACT. By an investigation based on corona discharge it is shown that there is a fixed constant, the true breakdown strength of the gas, for all types of gas discharge at normal pressures.

§ 1. INTRODUCTION

THE discharge of electricity through gases has been investigated generally with gases at low pressures, of the order of a few millimetres or less of mercury, and theories of ionization have been suggested to account for the phenomena observed. These theories have been concerned with the coefficients of ionization, α and β, of the ions contributing to the discharge, the measurements of which are possible at low pressures but not at normal or atmospheric pressures. At the low pressures the phenomena are further complicated by reason of the contribution of both positive and negative[1] ions to the discharge, and by photoelectric effects[2] both at the electrode surface and in the gas itself. For discharge at normal and high pressures, on the other hand, it is generally admitted that the electrons are the predominating source of ionization, and that photoelectric effects are neither present nor effective in the discharge. It would seem, therefore, that an experimental study of electrical discharge at normal gas-pressures should result in phenomena susceptible of a simpler explanation than the complicated phenomena at low pressures.

α, β

Up to the present, experimental work on electrical discharge in gases other than air at normal pressures has not led to any simple laws of discharge, or shown any uniformity or correlation between the results for different gases that might lead to a satisfactory explanation of the phenomena. This is because in the work that has been performed on sparking potentials there are at present no accurate empirical formulae representing the general conditions for discharge.

Much work however has been done on the discharge in air at normal temperatures and pressures, chiefly by electrical engineers in high-voltage technique, and has resulted in accurate empirical formulae that, to express the results, introduce a term familiarly called the "breakdown strength" of the gas. The fact that the "breakdown strength" is found to vary with the type of discharge, corona or sphere-gap, in the same gas, would seem to discredit to some extent the conception of "breakdown strength." If there is a definite breakdown constant for a given gas,

what is it and how is it determined? It will be shown in the present paper that provided one starts with a study of corona discharge in gases, for which the empirical laws are extraordinarily accurate and simple, and then proceeds to the study of spark discharge, it becomes possible to answer the above question, and to state definitely that there is a fixed constant, the true breakdown strength of the gas, holding for all types of discharge in the gas at normal pressures.

The study of corona discharge leads to fundamental laws that are the basis of the correct explanation of electrical discharge in gases, and these laws apply to sparking phenomena, although less accurately.

The present paper will be confined to an account of an experimental study of the various types of discharge in gases at normal pressures, their general correlation, and a statement of the fundamental laws of discharge derived from the work. Theoretical considerations of the results must remain for a future paper.

§ 2. GENERAL CONSIDERATIONS OF ELECTRICAL DISCHARGE AT NORMAL PRESSURES

The subject of electrical discharge in gases at normal pressure and temperature may be divided into two principal groups, viz. (a) local or corona discharge, occurring around conductors raised to sufficiently high potentials, but not extending to the opposite electrode or to earth; (b) spark discharge, consisting of complete electrical breakdown of the gas between the electrodes, and, unlike arc discharge, independent of the material of the electrodes.

Corona discharge has been investigated experimentally with three principal variations of electrode-shape and stress-distribution, namely (1) on wires and cylinders within coaxial cylinders, an arrangement very well suited to experimental investigation and to theoretical interpretation, and of practical use in the corona voltmeter; (2) on parallel wires, occurring in practice on overhead high-tension transmission lines; (3) on spheres at large spacings. Spark discharge, although it has been investigated with a diversity of shapes and sizes of electrodes, may be confined to the following types: (1) between equal spheres, an extremely important arrangement for the measurement of high peak voltages up to 1,500,000 V.; (2) between needle points, occasionally used for the measurement of peak voltages up to about 30 kV.; (3) between electrodes of shapes giving uniform-field conditions.

These types of discharge are similar with respect to certain fundamental conditions, which are of such importance in connexion with the work to be described in the present paper that a detailed statement of them is essential. They are as follows:

(1) At ordinary frequencies (say 10 to 500 ~) the experimental results for the critical establishment of all discharges are independent of frequency[3]. Moreover, the discharges are maximum-voltage phenomena, the results being generally the same for maximum alternating voltages as for direct voltages, positive and negative.

(2) The discharge is dependent only on the nature of the gas between the electrodes. It is independent of the material of the electrodes[4], provided they are clean, and in general of external sources of ionization such as ultraviolet or photo-electric effects[2]. Ionization contributing to the discharge is therefore gaseous and differs from arc discharge or discharge at low pressures, in which the electrode surfaces play a material part in the formation of the discharge.

(3) Paschen's law[5] is obeyed under all conditions. This, the basic law of electrical discharge, states that the disruptive voltage is a function of the mass of gas between the electrodes, and is therefore independent of the temperature and pressure of the gas except in so far as they alter the density. Temperature ionization of the Saha type is absent or negligible therefore in electrical discharge up to at least 860° C., the highest temperature reached in experimental verifications of Paschen's law[7].

The independence of electrical discharge upon the temperature and pressure of a gas, except in so far as they produce alterations in the gas-density, has been so conclusively proved in the cases of corona discharge in air and spark discharge in many gases that, in the experimental work to be described in the present paper, it has not been considered necessary to investigate temperature-changes, and variations of gas-density are effected solely by pressure-changes at atmospheric temperature.

§ 3. LAWS OF ELECTRICAL DISCHARGE IN GASES

For corona discharge on coaxial cylinders, parallel wires and spheres with large spacings (i.e. with spacing/radius ratio greater than about 2), and to an approximate degree for sphere-gap spark discharge (with spacing radius ratio greater than 0·25 but less than 2·0), the critical condition for the establishment of the discharge has been determined experimentally, and is of the form

$$G_m = G_0\rho \left\{1 + B\,(r\rho)^{-\frac{1}{2}}\right\} \qquad\qquad \ldots\ldots(1),$$

G_m, r where G_m is the maximum gradient at the surface of the electrode, of radius r, upon which the discharge begins, and is usually expressed in kV. cm. (crest value);
ρ, G_0 ρ is the density of the gas, referred to an arbitrary value of unity, G_0 the so-called
B "breakdown strength" of the gas, a constant for the gas at unit density, and B the "energy distance factor." G_m and G_0 are peak kilovolts throughout the paper.

The density ρ is taken to be unity at 760 mm. of barometric pressure, and either zero or normal temperature, and is therefore not the mass per unit volume but is merely a measure of the molecular concentration.

Equation (1) was first written in this form by Peek[8], who, in order to account for the fact that the discharge did not begin when the gradient became $G_0\rho$, intro-duced the idea of "energy distance" or "storage energy distance," without specify-ing its nature, and chose empirical relations of it with the gas-density and wire-radius to account for the equation.

In the experimentally observed values for G_0 and B in the case of air, however, these constants are found by Peek and others to vary in magnitude with the type

of discharge, having the following values in air respectively for corona on coaxial cylinders[9], corona on parallel wires[10], and sphere-gap spark discharge[11]:

$$G_m = 30 \cdot 5\, \rho\, \{1 + 0 \cdot 305\, (r\rho)^{-\frac{1}{2}}\},$$
$$G_m = 30 \cdot 1\, \rho\, \{1 + 0 \cdot 301\, (r\rho)^{-\frac{1}{2}}\},$$
$$G_m = 27 \cdot 2\, \rho\, \{1 + 0 \cdot 54\, (r\rho)^{-\frac{1}{2}}\}.$$

The differences in the "breakdown strength" term have thrown considerable doubt on its significance, whilst the fact that the "energy distance" does not become infinite for plane electrodes has discredited to some extent the conception of this term.

The first object of the present work was to investigate the different forms of discharge and to correlate if possible the different results obtained. By examination of corona discharge in many gases, for which the empirical relation (1) is well established, and comparison of the results obtained with previously published information on sparking-potentials in the same gases, such a correlation might be made possible. At the same time it was thought that further light might conceivably be thrown on the nature of the "breakdown strength" and "energy distance" and of ionization in gases at normal pressures.

§4. CORONA DISCHARGE

The results obtained for sparking-potentials between spheres, points, or plane electrodes, are identical whether the applied voltage be unidirectional (positive or negative) or alternating: in the latter case, the maximum value of the voltage wave is measured or taken, since spark discharge, like corona discharge, is a peak-voltage phenomenon, and independent of the frequency. With corona discharge, not only do the voltages differ slightly in the three cases, but also the nature of the glow itself does so. Positive corona glow is sharply defined and confined to a small region near the conductor; negative corona is diffuse, extending relatively far into the gas surrounding the electrode, and may occur at higher or lower voltages than positive corona; its occurrence depends, in a manner as yet not fully explained, on the nature of the gas, the gas-density, and the size of the electrode. Alternating-current corona discharge occurs at voltages that are approximately the mean of the results for positive and negative glow, and may have the physical characteristics of either positive or negative glow, or be a mixture of both; it depends on the gas.

Thus, for corona discharge in air at normal pressures, on wires ranging in radii from 0·37 to 0·116 cm., Whitehead and Brown[12] give the following results:

Positive corona: $\qquad\qquad G_m = 33 \cdot 7\, \rho\, \{1 + 0 \cdot 241\, (r\rho)^{-\frac{1}{2}}\},$

Negative corona: $\qquad\qquad G_m = 31 \cdot 02\, \rho\, \{1 + 0 \cdot 307\, (r\rho)^{-\frac{1}{2}}\},$

Alternating-current corona: $\quad G_m = 33 \cdot 7\, \rho\, \{1 + 0 \cdot 263\, (r\rho)^{-\frac{1}{2}}\},$

where r is in cm., and the density ρ is referred to a value unity at 25° C. and 760 mm. of gas-pressure.

Schumann[13] gives as the mean of all experimental data on positive and negative corona discharge in air,

$$+\text{ve } G_m = 31 \cdot 6\,\rho\,\{1 + 0 \cdot 268\,(r\rho)^{-\frac{1}{2}}\},$$

$$-\text{ve } G_m = 35 \cdot 0\,\rho\,\{1 + 0 \cdot 230\,(r\rho)^{-\frac{1}{2}}\},$$

and Whitehead[14], for alternating-current corona,

$$G_m = 30 \cdot 5\,\rho\,\{1 + 0 \cdot 305\,(r\rho)^{-\frac{1}{2}}\}.$$

These results for air, and perhaps more particularly those of Lee and Kurrelmeyer[15] on direct-current corona discharge, in several gases at pressures ranging from 0 to 30 cm., show that the differences between the values of the constants G_0 and B in equation (1) for positive, negative and alternating-current corona, though they appear to be considerable, are yet small in comparison with the variations for different gases. An investigation of corona discharge with either of the three types of voltage should therefore yield results of sufficient accuracy to enable the meaning of, and possible relation between, G_0 and B to be determined.

The use of alternating voltages in the investigation of corona discharge throughout the present work was determined not only by the convenience and accuracy with which such voltages can be controlled and measured, but more particularly by the fact that Lee and Kurrelmeyer, in their experiments on direct-current corona discharge, obtained results which failed to satisfy any simple relation such as (1). With alternating voltages, however, and wires ranging in diameter from 0·05 to 0·20 cm., in gases at atmospheric temperature and with pressures ranging from 20 to 76 cm. mercury, the writer has found that equation (1) is obeyed accurately by all gases.

Since there still remains uncertainty as to the actual values of the constants in the equation for corona discharge in air, and since the apparatus used in the present investigation differed considerably from the accepted form of corona voltmeter, it was decided to calibrate the transformer supplying the voltages by standard sphere-gap spark discharge, rather than by previous values of corona discharge. This would seem an advantage, since the results for corona discharge in the various gases are to be compared with those for spark discharge.

§ 5. APPARATUS

For a complete description of the apparatus used in investigating corona discharge, the various factors (space charge, etc.) taken into consideration in the design of the tube, the methods of voltage supply, regulation and measurement, the reader is referred to a paper communicated by the writer to the *Journal of the Institution of Electrical Engineers*. A diagram of the corona tube is given in figure 1. With a voltage range on the transformer from 0 to 20 kV., ranges of wire-size and gas-density respectively from 0·05 to 0·2 cm., and 10 to 76 cm. of mercury, it was

possible to investigate the relation between G_m/ρ and $(r\rho)^{-\frac{1}{2}}$ for values of the latter from about 3 to 15, an extremely wide range.
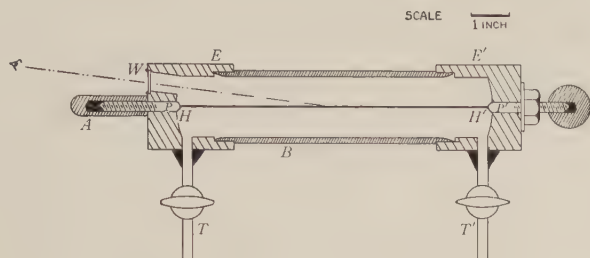
SCALE [1 INCH]

Figure 1. Diagram of corona apparatus.

§ 6. EXPERIMENTAL RESULTS

The colour of the discharge was pale purple or grey for all the gases investigated except carbon monoxide, in which the discharge was greenish in colour, especially at low pressures. When sparking occurred in the gases the sparks were sometimes vividly blue or red, the colour depending on the gas.

For air and oxygen the glow had the characteristics of positive corona, whilst for most of the other gases investigated in the present work—nitrogen, carbon dioxide, methane, hydrogen, nitrous oxide, ammonia, ethane, butane, pentane, and propane—negative-glow characteristics were present. Owing to the large values of the "energy distance" for some of the gases, and the fact that the glow extends into space to the same distance, it was extremely difficult to say definitely that any of the gases had a true negative glow; moreover, negative beads, a peculiarity of negative corona, were never obtained, since the voltage was not increased beyond the critical value for the establishment of the discharge. In the case of carbon monoxide, the discharge had none of the characteristics of either positive or negative corona, but in appearance was more like a brush discharge. The results obtained for this gas obeyed equation (1) to the same high degree of accuracy as did the results for the other gases, and have been included as being for corona discharge. Further, with this gas, local glow discharge did not occur when $(r\rho)^{-\frac{1}{2}}$ was less than about 4. The magnitudes of the sparking potentials for values of $r^{-\frac{1}{2}}$ equal to 3·55 and 3·205 accurately obey the law of corona formation which holds for values of $r^{-\frac{1}{2}}$ greater than 4·0, and are included in the results for this gas.

With nitrous oxide, the electrical discharge had a marked chemical effect upon the gas. If the usual precautions of renewing the gas after each observation are taken, the results obtained are not consistent, and the constants G_0 and B in the equation cannot be determined accurately. The most reliable method of obtaining the constants appeared to be not to remove the gas after each discharge; the effect due to chemical change is then smoothly cumulative. The values of the disruptive gradient at the initial density, for which there is little chemical change, could then be accurately determined from smoothed curves. Exact details of the method and results are too lengthy to be included in this paper, although some reference will be

made later to the nature of the chemical change. The effect of chemical change due to corona discharge is also noticeable in the case of air, but is absent for the rest of the gases, including the paraffins. In the case of oxygen, ozone is formed, which product appears to have the same critical breakdown properties as oxygen itself, for the results with oxygen are singularly consistent.

Peculiar results were observed at first with ammonia gas. This was obtained from dry liquid ammonia under pressure, further dried through tubes of phosphorus pentoxide, and the gas did not then react with the copper and brass of the apparatus. When first examined it gave an ill-defined brush discharge, upon which,
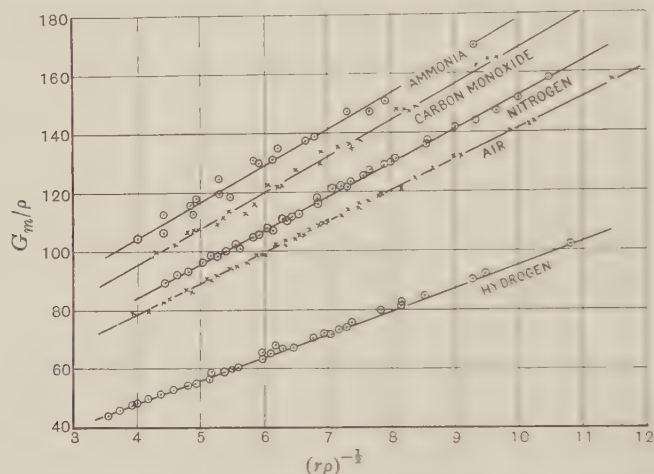
Figure 2. G_m/ρ, $(r\rho)^{-\frac{1}{2}}$ curves for corona discharge in ammonia, carbon monoxide, nitrogen, air and hydrogen. Points observed. Drawn curves calculated from the equations*

Ammonia: $\qquad G_m = 56\cdot7\rho\,\{1 + 0\cdot21\,(r\rho)^{-\frac{1}{2}}\}$.
Carbon monoxide: $G_m = 45\cdot5\rho\,\{1 + 0\cdot270\,(r\rho)^{-\frac{1}{2}}\}$.
Nitrogen: $\qquad G_m = 38\cdot0\rho\,\{1 + 0\cdot301\,(r\rho)^{-\frac{1}{2}}\}$.
Air: $\qquad\qquad G_m = 35\cdot5\rho\,\{1 + 0\cdot296\,(r\rho)^{-\frac{1}{2}}\}$.
Hydrogen: $\qquad G_m = 15\cdot5\rho\,\{1 + 0\cdot526\,(r\rho)^{-\frac{1}{2}}\}$.

$\rho = 1$ at $0°$ C., 760 mm.

as the voltage was increased, a true corona glow was superimposed. Results for the appearance of corona obtained in this way were at first irregular. The phenomenon (which was not observed with carbon monoxide, for which gas the brush discharge was well defined) seemed to be purely fortuitous, and was not always repeated even under apparently identical conditions. On repetition of the experiments, true corona-discharge results were obtained, the discharge being free from brush-discharge characteristics.

The experimental results for the various gases are shown graphically in figures 2, 3, 4, 5, and have been represented in the customary $G_m\,\rho$ and $(r\rho)^{\frac{1}{2}}$ linear relations. In the calculation of the constants G_0 and B in equation (1), G_0 is given in kilovolts

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* The initial constants in these equations, and in corresponding equations throughout the paper, have been revised since the paper was first submitted, an error having been found in the high-tension voltmeter used for the measurements.

per centimetre (crest values), r is in centimetres, and ρ is referred to a density of unity at $0°$ C. and 760 mm. of pressure for all gases. It will be seen that the relations

Figure 3. G_m/ρ, $(r\rho)^{-\frac{1}{2}}$ curves for corona discharge in ethane and methane. Points observed. Drawn curves calculated from the equations

$$\text{Ethane:} \quad G_m = 37 \cdot 2 \rho \{1 + 0 \cdot 344 \, (r\rho)^{-\frac{1}{2}}\}.$$
$$\text{Methane:} \ G_m = 22 \cdot 3 \rho \{1 + 0 \cdot 585 \, (r\rho)^{-\frac{1}{2}}\}.$$

$$\rho = 1 \text{ at } 0° \text{ C., 760 mm.}$$

Figure 4. G_m/ρ, $(r\rho)^{-\frac{1}{2}}$ curves for corona discharge in pentane, butane, propane and oxygen. Points observed. Drawn curves calculated from the equations

$$\text{Pentane:} \ G_m = 63 \cdot 1 \rho \{1 + 0 \cdot 225 \, (r\rho)^{-\frac{1}{2}}\}.$$
$$\text{Butane:} \quad G_m = 47 \cdot 7 \rho \{1 + 0 \cdot 263 \, (r\rho)^{-\frac{1}{2}}\}.$$
$$\text{Propane:} \ G_m = 37 \cdot 2 \rho \{1 + 0 \cdot 322 \, (r\rho)^{-\frac{1}{2}}\}.$$
$$\text{Oxygen:} \ G_m = 29 \cdot 1 \rho \{1 + 0 \cdot 401 \, (r\rho)^{-\frac{1}{2}}\}.$$

$$\rho = 1 \text{ at } 0° \text{ C., 760 mm.}$$

between G_m/ρ and $(r\rho)^{-\frac{1}{2}}$ are linear for all the gases, as is suggested by equation (1), and no departures from linearity such as those given by other experimenters, e.g.

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Brooks and Defandorf, and Whitehead and Isshiki[6], were observed under the conditions of experiment.

The results for the gases which were obtainable in quantity are probably accurate to within 1 per cent, although errors of this order are introduced in the methods of computing the values of the constants G_0 and B. For those gases which were not obtained in sufficient quantity to allow of fresh gas being admitted to the chamber after each observation, the results can be relied upon to about 2 per cent. The large experimental errors in ethane from the drawn curve may be attributed to the fact that only a very small quantity of the pure gas was available for experimental purposes.
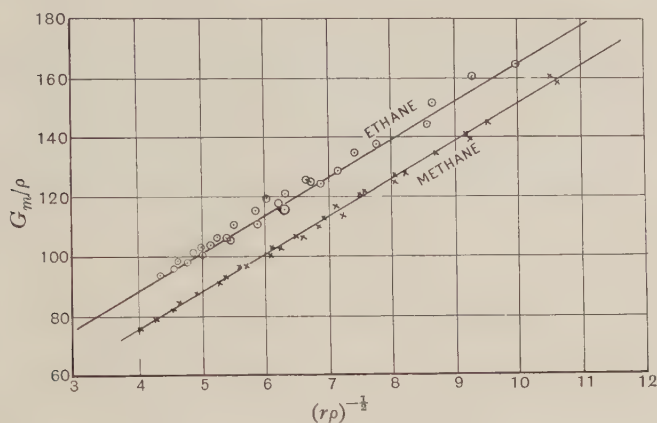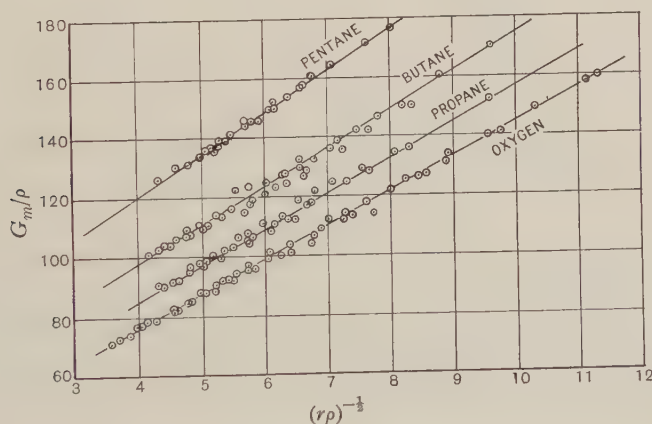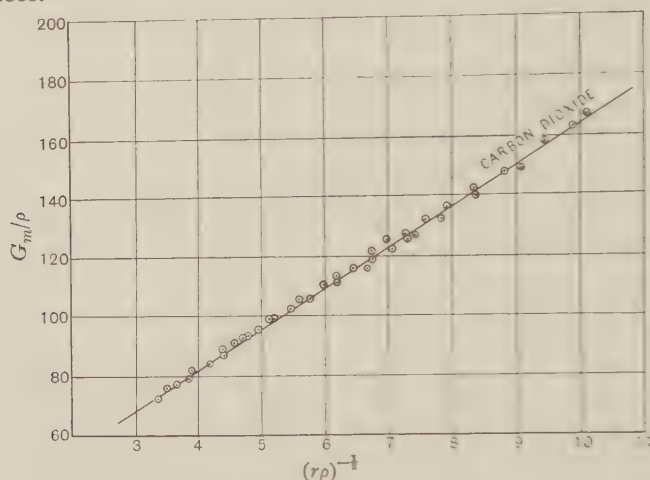

Figure 5. G_m/ρ, $(r\rho)^{-\frac{1}{4}}$ curves for corona discharge in carbon dioxide. Points observed. Drawn curve calculated from the equation

$$\text{Carbon dioxide: } G_m = 26\cdot2\,\rho\,\{1 + 0\cdot525\,(r\rho)^{-\frac{1}{4}}\}.$$

$$\rho = 1 \text{ at } 0^\circ \text{ C., } 760 \text{ mm.}$$

In table 1 the results are given for the breakdown strength and "energy distance" factor for the thirteen gases investigated. It is well known that corona discharge is a phenomenon occurring with great suddenness as the voltage is raised. It is this that enables observations to be taken with the remarkable consistency shown by the curves.

Table 1. Constants at 0° C. and 76 cm. for corona discharge in gases

Gas	G_0(kV./cm.)	B	Gas	G_0(kV./cm.)	B
Air	35·5	0·296	Hydrogen	15·5	0·526
Ammonia	56·7	0·210	Oxygen	29·1	0·401
Nitrogen	38·0	0·301	Ethane	37·2	0·344
Carbon monoxide	45·5	0·270	Butane	47·7	0·263
Nitrous oxide	55·3	0·275	Propane	37·2	0·322
Carbon dioxide	26·2	0·525	Pentane	63·1	0·225
Methane	22·3	0·585			

§ 7. THE RELATION BETWEEN THE "BREAKDOWN STRENGTH" AND "ENERGY DISTANCE" FACTOR

The values of the coefficients G_0 and B are plotted against each other in figure 6. In the graph a the curve is drawn for G_0B = constant = 12·3, and in the latter b, a graph of G_0 against B^{-1}. The equation to the drawn curve is $G_0 = 12·3\, B^{-1}$. Such curves are sufficient to show the close relation between G_0 and B. The departures are small, except in the cases of hydrogen and nitrous oxide, and are undoubtedly due to the fact that the glow may have positive, negative, or alternating-current corona, or brush-discharge characteristics.
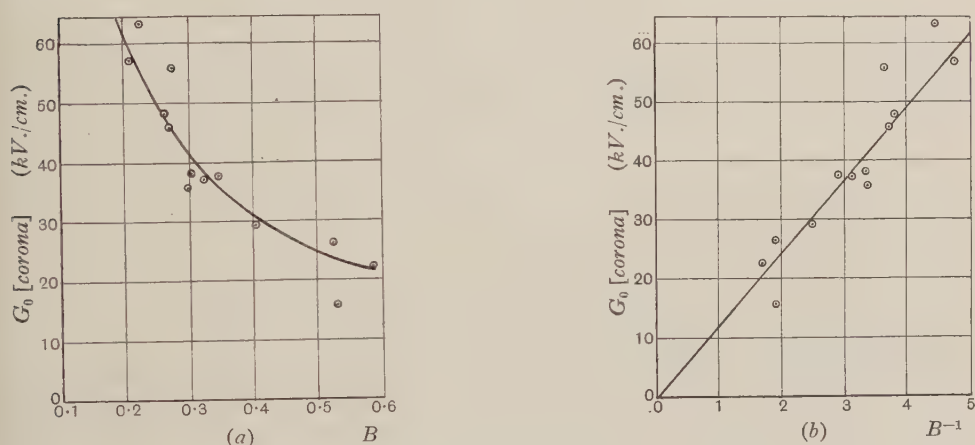
Figure 6. Graph showing the relation between the "breakdown strength" G_0 and the "energy distance" factor B. The drawn curves are calculated from the equations

(a) G_0B = constant, 12·3.

(b) $G_0 = 12·3/B$.

The relation G_0B = constant holds only when the gases are referred to unit densities at the same pressure and temperature, and does not hold when the actual densities of the gases are considered. Apparently, then, the relation is tenable only when the gases have the same number of molecules per unit volume. Since the actual number of the molecules rather than any specific property appears to determine the relation above, it follows at once that temperature and pressure should have no intrinsic effect on the breakdown properties except in so far as they alter the molecular concentration or density. This, as has previously been mentioned, is one of the fundamental laws of electrical discharge, Paschen's law.

If use be made of the above experimentally observed fact, the equation for *corona discharge* in gases becomes

$$G_m = G_0\rho + Y\,(\rho/r)^{\frac{1}{2}} \qquad \qquad \ldots\ldots(2),$$

where Y is a constant approximately *the same for all gases*. This equation is the

Y

first to show any marked unity amongst the different gases in the phenomena of electrical discharge through them at normal pressures, and is the key to the explanation of the effect.

§ 8. SPHERE-GAP SPARK DISCHARGE

In a previous paper[16], the writer has shown that if

$$G_m = G_0\rho \{1 + B\,(r\rho)^{-\frac{1}{2}}\}$$

represents the condition for corona discharge on coaxial cylinders for a given gas, then the condition for sphere-gap spark discharge in the same gas, for values of the spacing/radius ratio greater than 0·25, could be written

$$G_m = kG_0\rho \{1 + k'B\,(r\rho)^{-\frac{1}{2}}\} \qquad \qquad \ldots\ldots(3),$$

k, k' where k and k' have the *same values for all gases*, 0·89 and 1·60 respectively. For sphere-gap spark discharge, therefore, equation (3) takes the form

$$G_m = kG_0\rho + X\,(\rho/r)^{\frac{1}{2}} \qquad \qquad \ldots\ldots(3a),$$

X where X is the same constant for all gases, but has not the same value as Y in equation (2) above for corona.

§ 9. UNIFORM-FIELD SPARK DISCHARGE

Much experimental work has been done on sparking potentials in uniform fields in gases at normal pressures, and various formulae have been proposed to account for the phenomena observed. It may be stated that many of these formulae are unsatisfactory, often being purely empirical and having no correlation with the laws of corona and sphere-gap spark discharge. The laws developed by Townsend and Schumann, however, do attempt to correlate the different kinds of discharge, and will therefore be considered here in detail.

Townsend[17], in explaining corona laws, correlates sparking potentials for uniform fields with corona discharge. He assumes that ionization by collision takes place between the corona-forming electrode and the place where the gradient is equal to the value of the breakdown strength, and that a spark passes between the two boundaries. His argument is as follows:

For the case of wire and cylinder,

$$G_m = \frac{V}{r \log_\epsilon (R/r)},$$

$$G_0 = \frac{V}{(r + c) \log_\epsilon (R/r)},$$

G_m, r, G_0 where G_m is the gradient at the surface of the inner cylinder, of radius r, and G_0 the
c gradient at a distance c, the "energy distance" from the surface of the inner cylinder.

Therefore $\dfrac{G_m - G_0}{G_0} = \dfrac{c}{r}$ $\ldots\ldots(4).$

The sparking equation for uniform fields is assumed to be

$$G_{mean} = G_0 + D/S \qquad \qquad \text{......(5)},$$

where G_{mean} is the applied voltage/spacing, S the sparking distance in cm., G_0 the breakdown strength and D a constant.

G_m, S, G_0
D

From equations (4) and (5) we arrive at an equation for corona discharge, viz.:

$$G_m = G_0 \{1 + r^{-\frac{1}{2}} (2 D/G_0)^{\frac{1}{2}}\}.$$

In comparing sparking with corona, we should expect the best agreement between them under conditions for which the mean gradients—$\frac{1}{2} (G_m + G_0)$ in the case of corona and G_{mean} for sparking potentials—in each case are approximately equal, or the sparking distance and corona "energy distance" are equal. From this we are led to expect that sparking should be analogous to corona for spacings of the order o to 2 or 3 mm. In Keil's [18] determinations of sparking potentials V between spheres 1 cm. in radius, the field is uniform for spacings up to 2 or 3 mm., and for this range, if Townsend's theory is correct, the conditions for discharge should be representable by equations of the type

V

$$V = G_m S = G_0 S + \tfrac{1}{2} G_0 B^2 = G_0 S + D.$$

Analysing Keil's results, we find that this law is very nearly obeyed for air, oxygen, nitrogen, methane and carbon monoxide, but not in the cases of hydrogen and carbon dioxide. The results for the constants G_0 and D are given in table 2 together with those calculated from the writer's corona results, Townsend's theory being assumed to be correct. All results are given for density conditions of unity at 25° C. and 760 mm. pressure.

Table 2. Relation between V and S

Gas	Experimental results (from Keil)	Results calculated from corona
Air	$V = 34\cdot0\ S + 1\cdot40$	$V = 32\cdot5\ S + 1\cdot51$
Nitrogen	$V = 32\cdot0\ S + 2\cdot75$	$V = 34\cdot9\ S + 1\cdot72$
Oxygen	$V = 34\cdot0\ S + 0\cdot80$	$V = 26\cdot8\ S + 2\cdot34$
Methane	$V = 31\cdot5\ S + 0\cdot80$	$V = 21\cdot2\ S + 3\cdot50$
Carbon monoxide	$V = 39\cdot5\ S + 2\cdot50$	$V = 42\cdot7\ S + 1\cdot66$

It is at once apparent that so far as the "energy distance" term is concerned, there is no agreement between the two series of results, observed and calculated, nor can the results for the breakdown terms be regarded as satisfactory. Moreover, to obtain agreement with the corona law that

$$G_0 B = \text{constant},$$

it follows that for spark discharge in uniform fields,

$$G_0 D = \text{constant}.$$

There is no evidence of this in Keil's results. The above comparison of corona and spark discharge contrasts with the writer's comparison of corona and sphere-gap spark discharge, in which good agreement was obtained between the results of Keil and those of the writer [16].

Schumann[10] has proposed a theory of electrical discharge based upon a modified form of Townsend's fundamental law of discharge,

$$\int_0^l \alpha \epsilon^{\int_0^x (\beta - \alpha)} \, dx = 1.$$

The modified formula is

$$\int_0^l \alpha \, dx = K,$$

where α is the coefficient of ionization of the negative electrons and is a function of the electric field- and gas-density and l is the path over which ionization takes place.

For uniform-field spark discharge the gradient is constant, so that α also is constant, and the equation reduces to

$$\alpha \times \text{spacing} = K.$$

Schumann has proposed various formulae for the form of the function giving the dependence of the coefficient upon the field stress, such as

$$\alpha = \frac{A'}{G^2} \epsilon^{-B'/G^2},$$

$$\alpha = A'' \, \epsilon^{-B''/G^2},$$

$$\alpha = \frac{A'''}{G} \, \epsilon^{B'''/G^2},$$

where G is the stress, V/S, from which the equations for spark discharge become

$$\left. \begin{aligned} S &= \frac{G^2}{a'} \epsilon^{B'/G^2} \\ S &= \frac{1}{a''} \epsilon^{B''/G^2} \\ S &= \frac{G}{a'''} \epsilon^{B'''/G^2} \end{aligned} \right\} \qquad \ldots\ldots (5a).$$

Moderately good agreement with the results for air up to spacings of 10 cm. are obtained, but the values of the constants a and B are empirical, and differ widely in the various cases. Further, the correlation with corona and sphere-gap spark discharge is extremely laborious, and furnishes no evidence of the fundamental laws of discharge given in equations (2) and (3a) above.

As a result of an examination of the present results of corona and spark discharge, a new formula for sparking potentials in uniform fields has been found, holding in all gases for both spacing and gas-density variations, and correlating successfully with the results for corona and sphere-gap spark discharge. The theoretical derivation of this formula will be given in a future paper, and at present we shall content ourselves with an account of the experimental investigation of uniform-field spark discharge, and its correlation with corona and sphere-gap spark discharge.

In the present paper it is not proposed to give a detailed account of the apparatus used, and the design of the electrodes necessary to ensure uniform-field sparking,

but the reader is referred to a paper by the author in which apparatus and voltage-measurement are discussed at length [16]. Experiments were performed with a voltage range 0 to 60 kV. maximum values, giving a range of spacing at atmospheric pressure of 0 to 2 or 3 cm., depending upon the gas. Density variations at fixed spacings also were investigated with several of the gases. A diagram of the apparatus is shown in figure 6a.
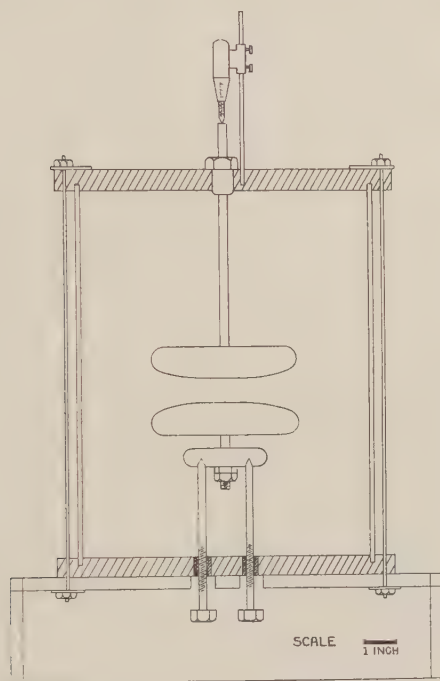
Figure 6 (*a*). Diagram of spark-discharge apparatus.

For all gases, the results were found to be represented by the equation

$$G_{\text{mean}} = G_0 \rho + Z \, (\rho/S)^{\frac{1}{2}}$$

or

$$V = G_0 \rho S + Z \, (\rho S)^{\frac{1}{2}},$$

where V is the applied voltage and $= G_{\text{mean}} S$, S is the spacing, ρ the density of the gas, referred for convenience in calculation in the present work to a value of unity at 25° C. and 760 mm. pressure, and Z a constant, independent of spacing and density.

The above formula holds accurately for all gases for variations of both density and electrode-spacing, and should be compared with the formulae of Townsend and Schumann [5, 5a]. In the case of air, the writer has found that it is obeyed for values of the disruptive voltage up to at least 425 kV. [16]

Experiments on sparking-potentials in uniform fields were performed upon the gases air, nitrogen, ammonia, carbon monoxide, hydrogen, carbon dioxide, methane and nitrous oxide, brass electrodes being used for all the gases with the exception

3

Table 3. Experimental results for spark discharge in uniform
fields at 0° C., 760 mm.

Gas	G_0(kV./cm.)	Z	Gas	G_0(kV./cm.)	Z
Air	26·6	7·84	Nitrous oxide	44·1	6·45
Nitrogen	27·8	7·35	Methane	21·2	8·56
Carbon monoxide	29·4	9·06	Ammonia	34·5	3·73
Hydrogen	14·4	5·86	Oxygen	32·5	3·47
Carbon dioxide	23·3	7·72			

Mean value of Z 7·54, omitting ammonia and oxygen.
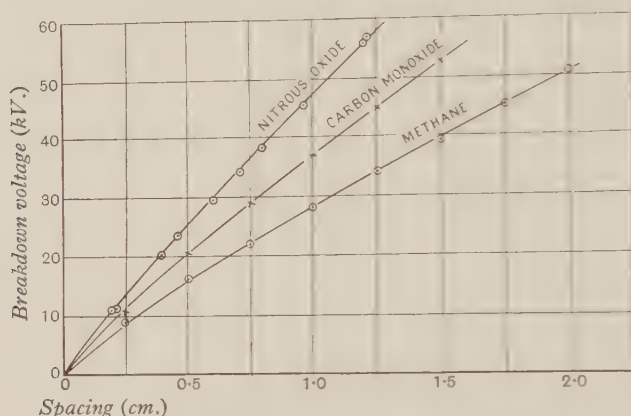
Figure 7. Spark discharge in nitrous oxide, carbon monoxide, and methane. Points observed. Drawn
curves calculated from the equations

Nitrous oxide: $V = 40\cdot3\,S + 6\cdot19\,S^{\frac{2}{3}}$.
Carbon monoxide: $V = 27\cdot9\,S + 8\cdot69\,S^{\frac{2}{3}}$.
Methane: $V = 19\cdot5\,S + 8\cdot20\,S^{\frac{2}{3}}$.

25° C., 760 mm.

of ammonia, in which case steel electrodes had to be substituted. The passage of a
spark through methane, for spacings greater than about 2 mm., resulted in chemical
decomposition of the gas, with the formation of soot deposit. The latter had a very
marked effect upon the breakdown voltage, lowering it by from 30 to 50 per cent.
The procedure with this gas was to polish the plates, pass sparks in air until con-
sistent observations were obtained, exhaust and refill the apparatus with methane,
and apply the voltage to breakdown. This had to be repeated for every single ob-
servation, and resulted in the expenditure of 30 cubic feet of pure gas before a curve
such as that shown in figure 7 was obtained.

The experimental results for the gases are shown in figures 7, 8, 9 and 10, show-
ing (voltage, spacing) relations, and in figures 11 and 12, in which (voltage, density)
variations for a few of the gases are given. The drawn curves are calculated from the
above formula, where G_0 and Z have values as given in table 3. In this table, how-

ever, the results are expressed in terms of a density of unity at 0° C. and 760 mm. pressure, for convenience in comparing them with the corona discharge results, whereas in the curves all results are for a density of unity at 25° C. and 760 mm., very nearly the density conditions under which the experiments were performed.
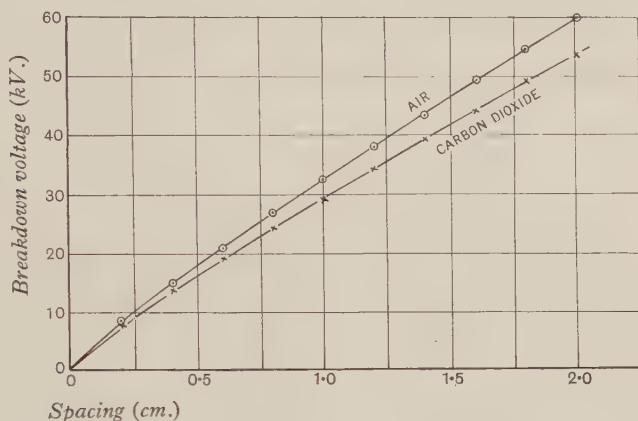
Figure 8. Spark discharge in air and carbon dioxide. Points observed. Drawn curves calculated from the equations

Air: $\qquad V = 24{\cdot}4\,S + 7{\cdot}50\,S^{\frac{1}{2}}$.
Carbon dioxide: $\quad V = 21{\cdot}4\,S + 7{\cdot}40\,S^{\frac{1}{2}}$.
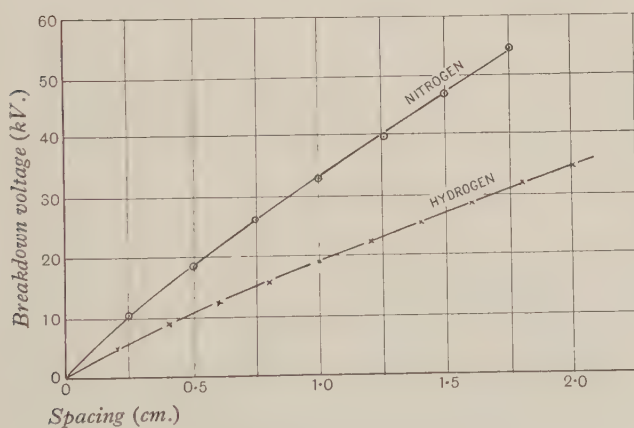
25° C., 760 mm.

Figure 9. Spark discharge in nitrogen and hydrogen. Points observed. Drawn curves calculated from the equations

Nitrogen: $V = 25{\cdot}5\,S + 7{\cdot}03\,S^{\frac{1}{2}}$.
Hydrogen: $V = 13{\cdot}2\,S + 5{\cdot}60\,S^{\frac{1}{2}}$.
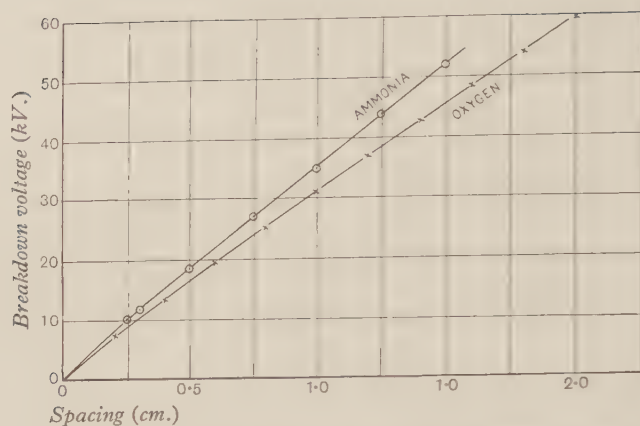
25° C., 760 mm.

Figure 10. Spark discharge in ammonia and oxygen. Points observed. Drawn curves calculated
from the equations
$$\text{Ammonia:} \quad V = 31\cdot6\,S + 3\cdot57\,S^{\frac{1}{2}}.$$
$$\text{Oxygen:} \quad V = 29\cdot8\,S + 3\cdot32\,S^{\frac{1}{2}}.$$
$$25^\circ \text{ C., 760 mm.}$$
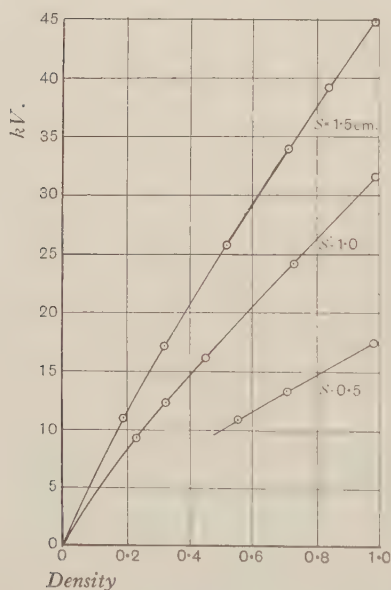
Fig. 11.

Fig. 12.

Figure 11. Spark discharge in air, showing variation of breakdown voltage with gas-density at fixed
spacings. Drawn curves calculated from the equation
$$V = 24\cdot4\,\rho S + 7\cdot50\,(\rho S)^{\frac{1}{2}},$$
where ρ is unity at 25° C. and 760 mm.
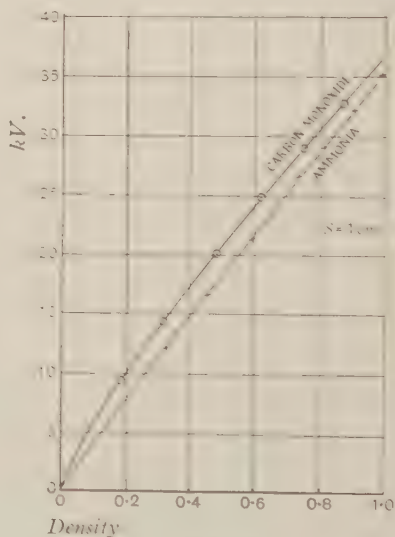
Figure 12. Spark discharge in ammonia and carbon monoxide, showing variation of breakdown voltage
with gas-density at a fixed spacing of 1 cm. Drawn curves calculated from the equations
$$\text{Ammonia:} \quad V = 31\cdot6\,\rho S + 3\cdot57\,(\rho S)^{\frac{1}{2}},$$
$$\text{Carbon monoxide:} \quad V = 27\cdot9\,\rho S + 8\cdot69\,(\rho S)^{\frac{1}{2}},$$
where ρ is unity at 25° C. and 760 mm.

§ 10. CORRELATION OF LAWS OF CORONA AND UNIFORM-FIELD SPARK DISCHARGE

In attempting to correlate the results for corona discharge on coaxial cylinders and spark discharge in uniform fields, attention must be paid not only to the break-down-strength terms in the different equations, but also to the so-called "energy distance" terms. It has been shown that the new conditions for *corona discharge* may be written

$$G_m = G_{0\,(\text{CORONA})}\, \rho \left\{ 1 + B\,(r\rho)^{-\frac{1}{2}} \right\},$$

where B is inversely proportional to G_0, whilst the equation for *uniform-field spark discharge* may also be written

$$G_{\text{mean}} = G_{0\,(\text{SPARK})}\, \rho \left\{ 1 + K\,(\rho S)^{-\frac{1}{2}} \right\}.$$

In this form, the equation is of interest in connexion with Peek's theory of energy storage[20], in which he assumed that the energy distance is proportional to the square root of the radius of the electrode, and inversely proportional to the square root of the gas-density, in which case the distance becomes infinite for plane electrodes, so that discharge should not occur. Actually, however, as has been shown experimentally above, the energy distance term for uniform-field discharge is inversely proportional to both the gas-density and the electrode-spacing.

The values of the breakdown strengths in the two equations are compared graphically in figure 13, from which it will be seen that we may write

$$G_{0\,(\text{CORONA})} = 1\cdot 25\, G_{0\,(\text{SPARK})}$$

representing a very definite relation between the two types of discharge.

Further, if G_{0_S} is plotted graphically against K, as in figure 14, it is also seen that G_{0_S} is approximately inversely proportional to K, except in the case of ammonia and oxygen—a relation similar to that found for corona discharge, although not of the same order of accuracy. The agreement is sufficient, however, to enable us to write as a first approximation, for uniform-field spark discharge in all gases,

$$G_{\text{mean}} = G_{0_S}\rho + Z\,(\rho/S)^{\frac{1}{2}},$$

where Z is a constant independent of the nature of the gas.

It will be shown theoretically in a future paper[21] that the breakdown strength obtained in uniform-field spark discharge is the true breakdown strength of the gas, so that if it be represented by G_0 for a given gas, it is now possible to summarize the conditions for the three important types of discharge as follows:

(1) *Uniform-field spark discharge.*

$$G_m = G_0\rho + Z\,(\rho/S)^{\frac{1}{2}}, \text{ where } Z = 7\cdot 54 \text{ at } 0°\text{ C., } 76 \text{ cm.}$$

(2) *Sphere-gap spark discharge.*

$$G_m = 1\cdot 11\, G_0\rho + X\,(\rho/r)^{\frac{1}{2}}, \text{ where } X = 17\cdot 5 \text{ at } 0°\text{ C., } 76 \text{ cm.}$$

(3) *Corona discharge on coaxial cylinders.*

$$G_m = 1\cdot 25\, G_0\rho + Y\,(\rho/r)^{\frac{1}{2}}, \text{ where } Y = 12\cdot 3 \text{ at } 0°\text{ C., } 76 \text{ cm.}$$

In the above formulae, the coefficients Z, X and Y are the same *for all the gases*, to a first approximation, the deviations from the constant value decreasing as we pass from spark discharge to corona discharge, in which latter case the constancy is exceptionally well defined.
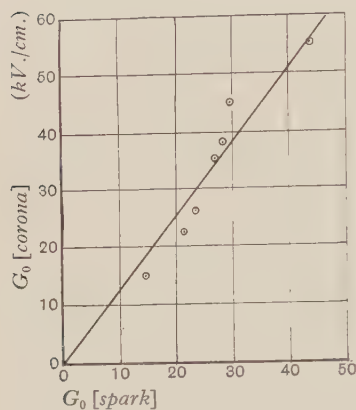
Figure 13.

Figure 14.

Fig. 13. Comparison of G_0 from corona discharge and G_0 from spark discharge. Drawn curve calculated from the equation

$$G_0\text{ (CORONA)} = 1\cdot 25\ G_0\text{ (SPARK)}.$$

0° C., 760 mm.
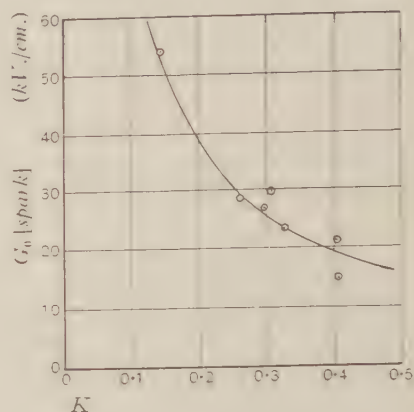
Fig. 14. Spark discharge in uniform fields. Graph showing the relation between G_0 and K. Drawn curve calculated from the equation

$$G_0 K = 7\cdot 54.$$

0° C., 760 mm.

These equations show at once the existence of a definite constant G_0 which is the breakdown strength of a gas, the satisfactory correlation of the different types of discharge, and also a fundamental unity in the sparking and discharge laws for all gases under all conditions. The physical significance and theoretical interpretation of these experimental results will be dealt with fully in a future paper.

§ 11. ACKNOWLEDGMENTS

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DISCUSSION

Dr L. SIMONS said that the breakdown of a gas depends on the velocity which the gas particles acquire in the electric field, in relation to the energy required for ionizing a molecule. In the case of a spark, a snowball effect takes place.

Dr R. W. LUNT. I would like to suggest that, in view of the importance of the paper, it would be unfortunate if it were published without the experimental details being described so that the accuracy of the work could be immediately appreciated.

With the exception of air, in which relatively little chemical change is produced, all the compound gases examined in the paper are readily decomposed by electric discharges: it is therefore very doubtful whether any of the curves, except those for hydrogen and nitrogen, can be accepted as referring to the gases to which they have been assigned.

The author might find it interesting to apply the general equations for discharges between coaxial cylinders and in uniform fields to his experimental data. If values of $G_m \rho^{-2}$ are calculated for hydrogen and nitrogen from equation (2) for $r = 0.05$, $\rho = 0.15$ to 1.0, and $G_0 = 15.5$ and 38.0 respectively, and if these values are then compared with the experimental values in figure 2, it will be seen at once that the discrepancies between the two sets of values are so great, particularly in

the case of hydrogen, that the validity of equation (2) is very doubtful. On the other hand, it is only fair to point out that if the same values are used for G_0, together with the relation $G_{0\,(corona)} = 1\cdot25\ G_{0\,(spark)}$, and taking $Z = 7\cdot54$, then the values calculated for $V = G_m S$ agree satisfactorily with the experimental values for hydrogen, and are only 10 per cent higher than those for nitrogen in uniform field discharges cited in figure 8.

AUTHOR'S reply. I appreciate Dr Lunt's remarks and agree that corona discharge does produce chemical changes in certain gases, for example the paraffins, ammonia, air and nitrous oxide. In work upon the electrical breakdown properties of gases, it is extremely difficult to allow for the effect of these chemical changes: this is evident from the remarks in the paper concerning the difficulties experienced in investigating corona discharge in nitrous oxide and spark discharge in methane. Moreover, since the product of the breakdown strength and energy distance factor $(G_0 B)$ is constant in the equation

$$G_m = G_0\rho\left[1 + B\left(r\rho\right)^{-\frac{1}{2}}\right] = G_0\rho + Y\left(\rho/r\right)^{\frac{1}{2}},$$

it is evident that any chemical change will only affect the electrical breakdown in so far as it alters the breakdown strength G_0, which will be altered to the true value for the new gas or mixture of gases. The change is small, as is shown by experiments on sparking potentials in gas mixtures, and further, since Y does not vary much for the different gases, and is by far the larger factor in determining the discharge voltage in the above equation, the electrical breakdown properties of any gas will not be altered appreciably by chemical changes in it. It was found in corona discharge in the gases oxygen, nitrogen, hydrogen, methane, carbon monoxide and carbon dioxide, that prolonged corona discharge did not appreciably affect the breakdown properties. Since the wires used were all of small diameter, the volume of gas in the corona glow is a very small proportion of the total volume of gas in the chamber, and the duration of the discharge is only about 2 seconds, the chemical change, if any, is small.

With regard to equation (2): this is clearly from the figure an approximate generalization of the results of corona discharge in the thirteen gases investigated, and the deviations from it are large in the cases of hydrogen, nitrous oxide and pentane. These errors do not affect the generalization that $G_0 B$ is constant in type, and are comparable in magnitude with the errors between the breakdown strengths as obtained from corona and from uniform-field spark discharge (figures 13 and 14).

Throughout the paper no extreme precautions have been taken regarding gas purity, though several of the gases obtained from the Shell Mex laboratory were very pure. The equations derived may serve as a guide in the investigation of corona in other gases.

A NEW TYPE OF FREE-PENDULUM CLOCK

By G. A. TOMLINSON, D.Sc.,

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ABSTRACT. A new method of taking accurately defined seconds signals from a pendulum is described, in which a photoelectric cell is used in conjunction with a special arrangement of multiple slits. This has been developed into a complete free-pendulum system, self-maintained *in vacuo* by means of electrostatic impulses and having a closely governed arc.

IN time-measurements of the highest precision one of the principal features which imposes a limitation on the accuracy is the uncertainty in the seconds or other signals provided by the standard clock. The Shortt clock, for example, supplies consecutive seconds derived from the slave pendulum which are subject to an irregularity amounting to about 0·004 sec. The Shortt clock installed at the National Physical Laboratory has been modified to provide additional signals controlled by the free pendulum. These are obtained from the motion of the impulse lever and therefore occur only at 30-second intervals. The impulse is applied to the pendulum at a point fairly near to the suspension, and this limits the precision of any individual signal to within about ± 0·002 sec. This error is undesirable when the signals are used in conjunction with a chronograph measuring time to within 0·0002 sec. At the same time the long interval between signals renders it less possible to utilize a group of consecutive signals to define the beginning and end of the measured duration with increased accuracy.

Neither of the above signals can be regarded as precise enough for certain measurements of time involved, for example, in the experimental study of the behaviour of clocks or of frequency standards. In such work it is desirable if possible to attain an accuracy of the order one part in 10⁸, and if this is to be achieved in a test of reasonable duration, such as two to three hours, the uncertainty permissible is only about 0·0001 sec. Some experiments have therefore been made with a new method of procuring more precise seconds signals from a pendulum, originally with a view to equipping the Shortt free pendulum with a device for this purpose. These experiments have proved successful and have further led to the development of a new type of free-pendulum clock which appears to have several advantageous features.

The method used for obtaining very sharply defined seconds signals is as follows. The pendulum at its lowest point carries a plate having a group of narrow slits; about 1 mm. away there is a fixed plate with an exactly similar group of slits; and a parallel beam of light is directed on to the plates. The two grills of slits coincide when the pendulum is passing through its position of rest, permitting a momentary

flash of light to pass through the slits sufficient to operate a photoelectric cell. The plates are rectangular pieces of glass with an opaque smoke film on one face, and the set of slits is provided by ruling with a fine point on the film. It is easy to produce identical grills by ruling the two plates at the same operation.

The distribution of the slits is of special importance and is such that at no position of the pendulum, other than its rest position, are there more than two slits of the grills in coincidence out of a total of twelve. The grid-bias potential of the valve used with the photo-cell can readily be arranged so that the light flux through only two slits has no appreciable effect, and the momentary full coincidence at the

Figure 1.

mid-point of the swing is thus a unique event in the pendulum cycle as regards the signal-receiving apparatus. By using such a multiple slit it is possible to obtain the same flux of light that would pass through a coarse single slit, combined with the extreme sharpness of the time-definition only possible with a fine slit.

The appearance of the grill of slits is shown by figure 1, which is a photographic reproduction of the actual plate used. It consists virtually of an irregular scale $\frac{1}{2}$ in. in total breadth, each slit being about 0·002 in. in width. The condition that never more than two slits shall coincide or even partially coincide is satisfied if the divisions of the scale are such that none of the 66 possible intervals is duplicated, and the minimum difference between intervals is not less than the slit-width. Suitable values for the successive subdivisions of such a scale are shown in the first column of table 1. The second column gives all the single intervals between ad-

jacent lines, and the further columns give the intervals formed by pairs, threes, etc., of the single intervals. It can be seen that no interval occurs twice and the difference between any pair is never less than the slit-width.

Table 1

0	1	2	3	4	5	6	7	8	9	10	11
18	18										
44	26	44									
108	64	90	108								
192	84	148	174	192							
234	42	126	190	216	234						
290	56	98	182	246	272	290					
326	36	92	134	218	282	308	326				
348	22	58	114	156	240	304	330	348			
422	74	96	132	188	230	314	378	404	422		
470	48	122	144	180	236	278	362	426	452	470	
500	30	78	152	174	210	266	306	392	456	482	500

The amount of light able to pass through the grills in any displaced position is, in fact, less than that which would be passed by the coincidence of a single pair of slits, since the motion of the pendulum is angular and the two sets of slits are not parallel except at the instant of maximum velocity. The fixed grill is mounted on a small carriage provided with levelling screws and with a suitable lateral adjustment. With the pendulum at rest the fixed grill can readily be adjusted optically to coincide with the swinging grill.

An experimental pendulum which has been set up to test this signal device has yielded promising results. The duration of the successive seconds was measured on a high-precision chronograph recently constructed* at the National Physical Laboratory. The following table of typical results gives the values of 40 consecutive seconds (the pendulum was not adjusted to beat exact seconds).

Table 2

1·0060	1·0061	1·0062	1·0061
1·0061	1·0062	1·0060	1·0061
1·0062	1·0061	1·0059	1·0061
1·0060	1·0060	1·0060	1·0063
1·0061	1·0063	1·0062	1·0060
1·0061	1·0061	1·0063	1·0060
1·0063	1·0061	1·0060	1·0062
1·0060	1·0061	1·0062	1·0062
1·0060	1·0063	1·0060	1·0061
1·0063	1·0062	1·0060	1·0061

The 10-in. pendulum used in these experiments was very imperfectly mounted and stood on an ordinary laboratory bench. The results obtained are sufficient to show that the method is capable of providing signals of great precision, and with a properly designed pendulum the uncertainty should not exceed 0·0001 sec.

The duration of the signal is easily calculated from the slit-width and amplitude

* *J. Sci. Inst.* 8, 21 (1931).

of swing. In the experiments described the semi-arc of the grill was 0·5 in. and the maximum linear velocity was therefore approximately π in. sec. The duration of the signal current from zero to a maximum is thus 0·002 π or about $\frac{2}{3}$ millisec., and it is possible to set the cross-hair of the reading microscope on the starting point of the recorded signal mark to within 0·0001 sec.

As an extension of these experiments a new type of free-pendulum clock has been developed and an experimental model has been made with the same 10-in. pendulum and found to operate in a satisfactory way. A diagram of the arrangement is shown in figure 2. The pendulum swings *in vacuo* in an exhausted case
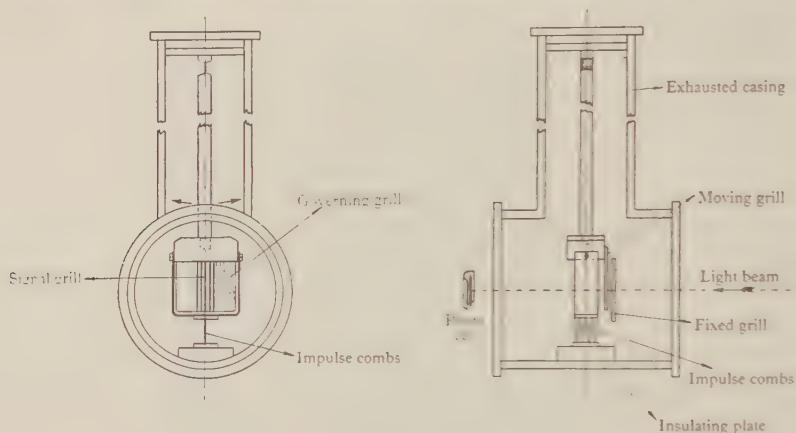
Figure 2.

constructed of thick-walled brass tube. The lower part has two plate-glass windows to allow the beam of light to pass right through the case and strike a photoelectric cell outside. The pendulum bob has the moving grill attached to it, and the fixed grill is shown diagrammatically, without details of the adjusting screws.

At its lowest point the pendulum carries a small comb composed of six parallel pieces of brass wire about 1·5 cm. in length. A similar fixed comb is adjusted to be in the same plane as the first comb when this is at rest, with the wires interleaved but not touching. When the pendulum is swinging one comb therefore passes freely through the other. These combs are used to give the pendulum a sufficient impulse at every swing, by means of an electrostatic force, to supply the lost energy. The impulse is controlled by the action of the photoelectric cell in such a manner that the amplitude of the pendulum is governed within close limits. For this purpose the plate attached to the pendulum is ruled with a second set of slits, shown in figure 2, to act as the governing grill. This is displaced from the signal grill by an angular rotation about the axis of the pendulum, equal to the amplitude of swing that is required. (The additional ruling of this grill presents no difficulties as it is only necessary to support the plate on a suitable radius arm.) The second grill thus comes into coincidence with the fixed grill at one extremity of the swing.

The general action of the impulsing and governing arrangements can be understood by reference to figure 3. Normally the fixed comb is charged through a high

resistance R_2 and as the pendulum in its swing approaches the mid-point, the combs come near enough together to exert some electrostatic attraction on each other. The force of attraction rises sharply to a maximum and then falls suddenly to zero when the planes of the two combs coincide. At this instant the photo-cell A receives the flash of light through the grills and this gives rise to a momentary anode current in the valve B associated with the cell. This operates a rapidly acting relay C which short-circuits the two combs for a moment and discharges the fixed comb. On continuing its motion past the mid-point, the pendulum carries its comb out of the range of attraction of the fixed comb without any appreciable force being exerted on it. The resistance, R_2, together with the small condenser C_2 across the combs, control the rate of charging as required. The cycle of events in one double swing of the pendulum is illustrated in figure 4. The impulse is shown just before the
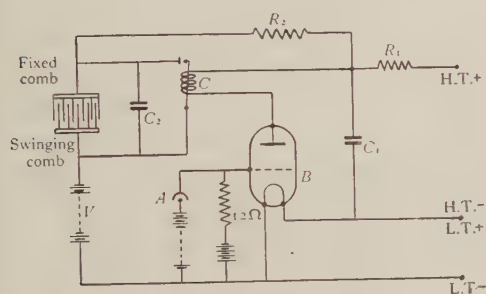
Figure 3.
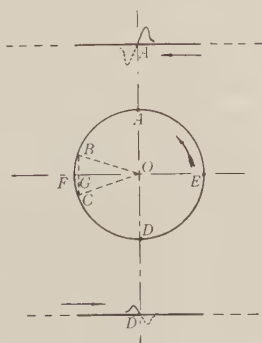
Figure 4.

pendulum arrives at the point A, the negative impulse which is eliminated by discharging the comb being shown as a dotted line. Continuing its motion to some point B very near the end of the swing, the governing grill now begins to open a passage for light to reach the cell, and at the extreme end of the swing the slits overlap by an amount FG. On the return swing the aperture closes again at C, and from B to C the valve is passing an anode current which rises to a maximum value at F. The anode is fed from a $2 - mF$ condenser C_1 which is connected to the h.t. supply through a high resistance R_1 so that it charges at a controlled rate. The result of partially discharging this condenser during the movement of the pendulum from B to C is, therefore, that the potential of the fixed comb when the point D is reached will depend on the potential difference across the condenser C_1. If a considerable discharge occurs from B to C owing to the amplitude tending to be large, the comb potential, and therefore the impulse at D, will be smaller than usual, and this checks the tendency of the amplitude to increase. By the time the pendulum has again reached the point A the p.d. across C_1 has built up to about its normal value, though some residual effect of an unusually large discharge may make itself felt as a slightly small impulse at A. The condenser C_1 is thus charged with a fluctuating potential which is automatically determined by the amplitude of the pendulum, and the reaction on the impulse maintains the amplitude at a constant value within limits which correspond to some fraction of the slit-width.

It is interesting to notice that the arc-governing device provides a further means of limiting the amplitude if it should tend to exceed the margin covered by the graduated control. An exceptionally large discharge of the condenser has the effect that when the point D is reached the condenser voltage is not sufficient to work the relay, and the impulse at D is thus cut out altogether. This action supplies an additional hit-and-miss safeguard against variation of amplitude, which normally does not require to operate when the magnitude of the normal impulse is correctly adjusted to be slightly greater than that required to supply the lost energy. This adjustment is made in a simple way by applying a suitable polarizing potential V to the moving comb as shown in figure 3.

The actual operation of the arc-controlling grill can usually be observed roughly on the chronograph record. The signals in both directions of motion are recorded, and it is generally seen that the signal at D is smaller in magnitude than that at A. It is at once obvious from the record when the hit-and-miss control comes into action. The chronograph marker may be connected in the anode circuit of the valve, but it is found equally satisfactory to place it in the output circuit of the relay so that it is operated by the discharge of the condenser C_2. In this position the seconds signals are of course subject to the additional uncertainty introduced by variations in the time of action of the relay. With the particular relay employed this is, however, a negligible amount, even in relation to the high precision obtained in the signals. The relay plays an important part in the maintenance of the pendulum, and it is clearly necessary that it should have the minimum possible time-lag. A special type of relay has been devised which has a time-lag not exceeding 0·0001 sec., the variations in which, as affecting the signals, are quite imperceptible. This relay is made by a small modification of a reed telephone movement. A light extension piece soldered to the reed carries a spherical-ended piece of platinum wire, which on the deflection of the reed comes into contact with a fixed plane piece of platinum. The reed responds with great rapidity, and the time interval between the input and output signals is actually too small to be measured on the chronograph.

The seconds signals obtained with the chronograph in the discharging circuit of the condenser C_2 are well-defined marks on the record, as would be expected. An example showing the type of signal is given in figure 5 which is a photograph of a portion of a chronograph record magnified 25 times. The parallel lines in pairs are traced by the two markers in the direction of the arrow, and the seconds signals from the pendulum are indicated by letters A. Comparison seconds from another clock are marked B. The traces seen are successive turns of a fine-pitched spiral of diameter about 150 in. on the scale of the figure, and ten signals have been recorded between the marks seen on adjacent traces. To give a scale to the record a series of radial lines have been ruled at intervals corresponding to 0·01 sec. It will be seen that the signals from the pendulum are sufficiently sharp for the cross-hair of the reading microscope to be set to within 0·0001 sec.

The general operation of the clock having been described, certain features of the scheme will now be considered briefly. The use of a pendulum *in vacuo* eliminates all effects of air-pressure, such as buoyancy and fluid friction. At the same

time the loss of energy per swing is very greatly reduced, so that, with an impulse applied regularly to every swing, the amount of energy to be supplied in one impulse is only an extremely small fraction of the energy of the pendulum. The impulse itself also approximately conforms to the ideal condition of occurring at the instant of maximum velocity. The electrostatic system of maintaining the pendulum renders the pendulum system less liable to disturbances from external causes than would be the case if electromagnetic forces were used. The signal system should have only a negligible reaction on the pendulum, from the point of view of the radiation pressure. All but a small fraction of the light is cut off by the fixed grill, and the fraction transmitted strikes the swinging grill in a direction normal to the plane of motion. In every respect, therefore, the motion very nearly approaches that of an ideal free pendulum.
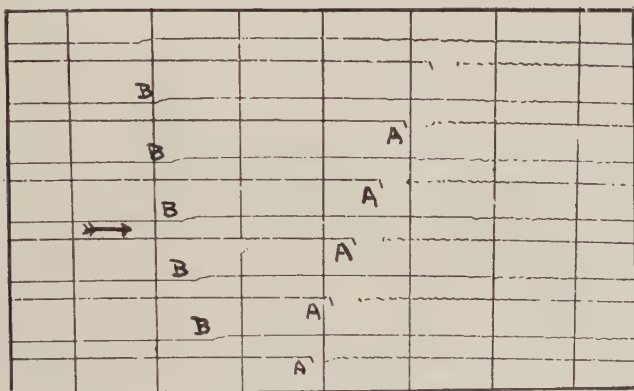
Figure 5. Portion of chronograph record (× 25).

The advantage gained by governing the arc within close limits is very well worth the slight additional complication involved, since variation of arc, from whatever cause it arises, is a primary cause of variation in rate. There is in fact no extra apparatus required for this purpose, the provision of the governing grill alone being sufficient. The scheme as a whole is really quite simple and direct, and has the considerable advantage that no slave clock is required. No difficulty arises in the occasional replacement of either the cell or the valve, or the illuminating lamp. The decrement of the pendulum *in vacuo* is so small that the driving may be interrupted while any of these components is changed, with a decay of amplitude altogether too small to have appreciable effect on the isochronism.

An important advantage of the clock as a laboratory instrument is the ease with which very accurate seconds signals can be taken direct from the free pendulum. The behaviour of the experimental model justifies the opinion that signals with a precision of 0·0001 sec. will be obtained with little difficulty. As regards the degree of isochronism possible with such a pendulum, no tests of any value can be made until a properly designed pendulum is available. It is proposed to install a new clock operating on this principle at the National Physical Laboratory in the same vault as the Shortt clock, and comparative tests of the two should prove of much interest.

DISCUSSION

Mr T. Smith asked whether the author had stabilized the governor so as to prevent any hunting effect and to keep the amplitude-corrections small.

Dr F. A. B. Ward. I should like to ask the author, firstly, whether it would be possible to displace the grids so that the impulse would reach its maximum at the exact centre of the pendulum's swing; and secondly whether he has considered the possibility of replacing the relay, or perhaps the whole system of triode valve and relay, by a gas-filled relay valve or thyratron. This substitution would, of course, involve redesigning the circuit. The thyratron would appear to be particularly suitable for use as a relay in exact time-measurement, as its time of response is less than 10^{-5} sec.

Prof. G. B. Bryan asked whether a small amount of air-damping was not desirable to facilitate control of the pendulum?

Author's reply. In reply to Mr T. Smith: I have as yet made no attempt to stabilize the arc-governing device. Until the final design of the clock is completed and working, it is impossible to decide whether such precautions will be necessary. The theoretical behaviour of the governing arrangement has been worked out to some extent, however, and the results indicate that the range of amplitude likely to occur as a periodic variation is not great enough to have an appreciable effect on the rate of the clock.

Dr Ward's suggestion to displace the impulse comb would be feasible as regards the impulse in one direction of motion, but would displace the next impulse in the opposite direction away from the centre of the swing. Possibly a more elaborate system using two fixed combs could be devised to do what he suggests, but it may be of interest to state that the calculated effect on the period of the pendulum of the asymmetry of the existing impulses is considerably under 1 part in 10^8. I am obliged to Dr Ward for suggesting the possibilities of the thyratron type of valve.

In reply to Prof. Bryan: I think it is desirable to have some constant air damping in the case of a pendulum maintained by an impulse of fixed magnitude. A balance has to be attained between the energy supplied in the impulse and the energy lost in the duration between the impulses. The arc of the pendulum automatically adjusts itself to procure this balance, and the probable variations in the arc are determined by the rate of change of the lost energy with respect to amplitude. The latter depends on the damping coefficient, which should not be reduced too much or instability of arc will be set up. When, however, the arc is governed, the impulse energy varies with amplitude at a rate which is many times greater than the rate of change of the lost energy, and it is the former which predominates in determining the closeness of control of the arc. The precision of the control is therefore adequate even when the pendulum is working with the smallest possible damping, a condition which is advantageous from all other points of view.

A PHOTOGRAPHIC METHOD OF DERIVING THE OPTICAL CONSTANTS OF THE METALS

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ABSTRACT. A grating consisting of alternate strips of glass and metal of known dimensions gives diffraction spectra whose relative intensities depend on the optical properties of the component parts. An expression has been found for the relative intensities of the central reflected image and the first principal diffracted image in terms of the reflection coefficients for the metal and glass and of the phase-change on reflection from the metal surface. By means of a photometric method which is described the intensity ratio has been measured for two or more gratings of different proportions cut on one mirror, enabling the deduction of the reflection coefficients and the change of phase to be made. This is done for light plane-polarized both in and perpendicularly to the plane of incidence, and the approximate Drude formulae are used to calculate the optical constants. It is possible to make simultaneous measurements at several wave-lengths if the grating is illuminated with light from a source having a suitable line spectrum. With gratings cut from sputtered platinum films, the means of six sets of results for the yellow doublet of the mercury arc were $k = 1\cdot40$ and $n = 1\cdot67$. An investigation is made of the most favourable conditions and the possibilities and limitations of the method are discussed.

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§ 1. INTRODUCTION

THE experimental methods employed during the past thirty years in investigating the optical properties of metals have followed in principle those introduced by Drude, and consist in a visual examination of the change produced in a beam of polarized light on reflection from a metallic surface.

In the procedure to be described advantage is taken of the more recently developed technique of intensity-measurement to enable the use of photographic observations of the light reflected and diffracted from specially ruled gratings. Whereas in the visual method monochromatic illumination is necessary, the following method makes possible the simultaneous measurement at several wave-lengths if a source having a suitable line spectrum is used.

Following a suggestion by Prof. Vonwiller, the effect of the polarization of the incident beam on the relative intensities of the diffracted images from a specially ruled grating was examined visually, and, with his help, a theoretical explanation was obtained. Further examination showed the possibility of using the effect as a means of investigating the optical properties of a metallic film. In this paper, published at this stage because the author may find it necessary to discontinue the work for a time, the technique so far developed and a few of the more satisfactory results are given.

4

§ 2. THEORY

Suppose that light is reflected from a diffraction grating composed of alternate strips of glass and metal (in the form of a film deposited on the glass). The intensity of the diffracted images relative to that of the central image will depend on the properties of the metal and of the glass as well as on the dimensions of the grating.

Let the grating be composed of alternate strips of glass of width b, and metal of width c, so that $b + c = d$, the grating constant. A plane wave diffracted from the glass strips will be described by the equation*

$$y = y_0 b \alpha \frac{\sin\left(\frac{1}{2}\mu b\right)}{\frac{1}{2}\mu b} \frac{\sin\left(\frac{1}{2}m\mu d\right)}{\sin\left(\frac{1}{2}\mu d\right)} \sin(\omega t + \epsilon) \qquad \ldots\ldots(1),$$

where α is the amplitude reflection coefficient for the glass. α can be calculated from a knowledge of the polarization of the initial beam, and we shall suppose that the light is plane polarized either in, or perpendicularly to, the plane of incidence. μ is a coefficient whose values are integral multiples of $2\pi d$ for the principal diffraction maxima. m is the number of strips.

The same wave diffracted from the metal strips will be described by the equation

$$y = y_0 c \beta \frac{\sin\left(\frac{1}{2}\mu c\right)}{\frac{1}{2}\mu c} \frac{\sin\left(\frac{1}{2}m\mu d\right)}{\sin\left(\frac{1}{2}\mu d\right)} \sin(\omega t + \epsilon + \theta + \delta) \qquad \ldots\ldots(2).$$

Here β is the amplitude reflection coefficient for the metal and δ the change of phase on reflection†. The addition of θ in the phase angle is due to the fact that the centres of the glass and metal strips are separated by a distance $\frac{1}{2}d$, and for the principal diffraction maxima $\theta = \pi$. ϵ is in each case a function of m.

The resultant vibration which gives rise to the first principal diffraction maximum will have an intensity I_1, where

$$I_1 = y_0^2 m^2 A^2 (\alpha^2 + \beta^2 - 2\alpha\beta \cos \delta) \qquad \ldots\ldots(3),$$

and

$$A = \frac{\sin(b\pi\,d)}{\pi/d}.$$

The intensity of the central image will be I_0, where

$$I_0 = y_0^2 m^2 (\alpha^2 b^2 + \beta^2 c^2 + 2\alpha\beta bc \cos \delta) \qquad \ldots\ldots(4).$$

By a photometric method we can measure the ratio of these intensities and obtain a value R, where $R = I_0/I_1$. We have, then,

$$R = \frac{\alpha^2 b^2 + \beta^2 c^2 + 2\alpha\beta bc \cos \delta}{A^2(\alpha^2 + \beta^2 - 2\alpha\beta \cos \delta)} \qquad \ldots\ldots(5).$$

This equation is a quadratic in β and $\cos \delta$ which are the only unknowns. We may calculate α by means of the Fresnel formulae, knowing the polarization, the

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* Drude, *Theory of Optics*, p. 222 (Eng. trans. 1902).

† The reflections from the metal and glass surfaces are not, of course, in the same plane and δ must therefore include the effect of path-differences. This question is discussed more fully below.

refractive index of the glass, and the angle of incidence; b and c are obtained by measurement and A is calculated from them. The value of m must be the same for both glass and metal, this being easily arranged by blacking out the undesired parts of the grating.

The quadratic equation is as follows:

$$\text{coefficient of } \beta^2 = RA^2 - c^2,$$

$$\text{coefficient of } \beta \cos \delta = -2\alpha(RA^2 + bc),$$

$$\text{constant term} = \alpha^2(RA^2 - b^2).$$

Now suppose we use two gratings of different proportions, distinguished by the suffixes 1, 2 and having the same constant d, so that $b + c_1 = b_2 + c_2$, and obtain R for each. We then have two equations of the form

$$p_1 x + q_1 y + r_1 = 0,$$

and

$$p_2 x + q_2 y + r_2 = 0.$$

Substituting for the coefficients p, q, r in the solutions of these the expressions given above, we obtain, after simplification, the formulae,

$$\frac{\beta^2}{\alpha^2} = \frac{A_1^2 R_1 b_2 - A_2^2 R_2 b_1 + b_1 b_2 (c_1^* - c_2)}{A_2^2 R_2 c_1 - A_1^2 R_1 c_2 + c_1 c_2 (c_1 - c_2)} \qquad \ldots\ldots(6),$$

and

$$\frac{2\beta \cos \delta}{\alpha} = \frac{(b_2 - c_2)(A_1^2 R_1 - c_1^2) - (b_1 - c_1)(A_2^2 R_2 - c_2^2)}{A_2^2 R_2 c_1 - A_1^2 R_1 c_2 + c_1 c_2 (c_1 - c_2)} \qquad \ldots\ldots(7).$$

These formulae are remarkably simple and compact. It is notable that the change of phase, δ, is calculable without a knowledge of α, although, of course, the latter's value greatly affects the magnitude of the quantities on the right-hand side.

The ratios R_1, R_2 are measured, and β and δ calculated for light polarized both in (s) and normally to (p) the plane of incidence. We then have the quantities β_p/β_s and Δ (in the notation of Drude), where $\Delta = \delta_p - \delta_s$. Putting $\beta_p/\beta_s = \tan \psi$ we may use the formulae given by Drude*, viz.

$$k = \sin \phi \tan 2\psi,$$

and

$$n = \sin \phi \tan \phi \frac{\cos 2\psi}{1 + \sin 2\psi \cos \Delta},$$

to obtain the optical constants. ϕ is the angle of incidence.

When the angle of incidence is greater than the polarizing angle for the glass, α_p changes sign. Since β is calculated from β^2/α^2 its sign is not known. Therefore β and β/α are assumed to be positive and the negative value of α is allowed for by adding $180°$ to δ_p, i.e. considering the wave to have been advanced through a half-period in its reflection from the glass surface. There is then ambiguity in the value of Δ, as to whether it is to be taken as $(180° + \delta_p + \delta_s)$ or $(180° + \delta_p - \delta_s)$. It is found that the value $(180° + \delta_p - \delta_s)$ gives the more reasonable results, which is perhaps to be expected since both δ_p and δ_s are then taken in the same sense.

* Drude, *loc. cit.* p. 363.

§ 3. PREPARATION OF GRATINGS

Preparation of mirrors. Only three sets of gratings have been prepared which give satisfactory results, one of silver and two of platinum. All were made by cathodic sputtering in vacuo, a sheet of foil covering the silver cathode in the case of the two latter. The sputtering method is limited, however, to a small range of metals and difficulty has been experienced in obtaining mirrors of the quality desired. In order to provide a means of depositing films of chromium, antimony, nickel, etc., which cannot be done by sputtering methods, apparatus has been designed for evaporating these metals in vacuo. Ordinary plate glass, free from scratches, is used for the mirrors in pieces about 6 cm. by 3 cm. in size.

Proportioning of gratings. On each mirror were ruled a number of gratings, each consisting of about forty strips at a spacing of 1 mm. and approximately 5 mm. in length. Although the theory indicates that only two gratings of different dimensions are necessary, it has been the practice to measure the intensity ratios from each of three gratings and, combining them in pairs, to obtain a mean value to which considerably more weight can be given.

Except in the case of the set of gratings last constructed it had been customary to cut three series of strips in which the width of the metal was 0·500 mm., 0·350 mm., and 0·200 mm. respectively; the choice being arbitrary and governed merely by a desire to obtain as large a variation in c as would be convenient. However, in the case of light polarized in the plane of incidence, E_s, the intensity ratios were high and difficult to measure and it was noticed that they increased as the width of the metal strip decreased. In an endeavour to obtain values of R as near to unity as possible, consistently with a wide variation in c, use was made of the more reliable of the results already obtained for β/α and R to investigate the connexion between the intensity ratio and the proportions of the grating.

Taking the first formula, equation (6),

$$\frac{\beta^2}{\alpha^2} = \frac{A_1^2 R_1 b_2 - A_2^2 R_2 b_1 + b_1 b_2 (c_1 - c_2)}{A_2^2 R_2 c_1 - A_1^2 R_1 c_2 + c_1 c_2 (c_1 - c_2)},$$

we may assume suitable values for R_1, b_1, c_1, A_1, and β/α. This then becomes a relation connecting R_2 as dependent variable with b_2, since $(b_2 - c_2)$ is constant. When R_2 is plotted against b_2 the curve will be roughly parabolic since the above equation is of the second degree in b_2 if the slow change in A_2 is neglected, so that there will be a minimum for R_2 at some value of b_2 near the middle of its range. Curves are given for both the plane of incidence E_s, figure 1, and the plane E_p normal thereto, figure 2, the constants assumed being taken from actual results.

When the electric vector is perpendicular to the incident plane E_s, figure 1, the minimum value of R_2 occurs when b_2 is approximately 0·550 mm. and the ratio rises rapidly outside the range $0·350 < b_2 < 0·650$. In the last mirror cut a set of strips in which $b_2 = 0·350$ mm. was therefore included.

In the case of E_p, figure 2, it will be seen that the value of R^{-1} rises rapidly in the range $0·650 < b_2 < 0·750$. To avoid this difficulty b must be at least 0·800 mm. in one of the gratings, so that the original dimensions were satisfactory.

Naturally previous results can only be used to design a fresh set of gratings if both mirrors have been prepared under similar conditions and are expected to give
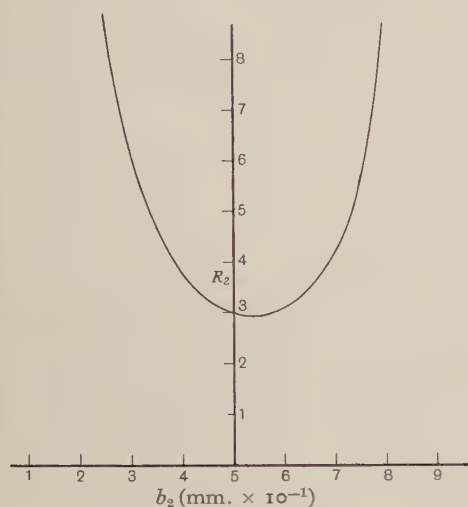
Figure 1.

Figure 2.

Figure 1. Intensity ratio as a function of the proportions of the grating. Electric vector normal to plane of incidence.
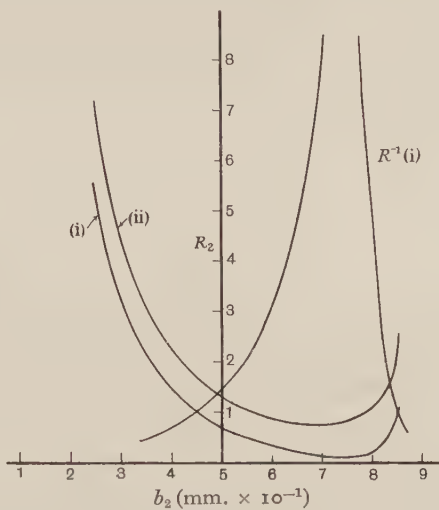
Figure 2. Intensity ratio as a function of the proportions of the grating. Electric vector parallel to plane of incidence.

similar effects. The discussion is interesting since it illustrates the possibility of using a grating in which the metal strip is wider than the glass. It is to be noted also that the interchange of b and c will not leave the value of R unchanged.
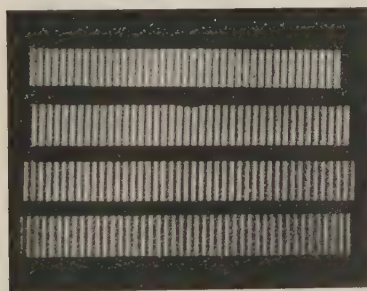
Figure 3. Contact print of second set of platinum gratings, showing variation in b and c. The darker strips are of metal.

Ruling. As will be seen later it is desirable that the width of the strips should be accurate to at least 0·002 mm. and, if possible, to 0·001 mm. The gratings have been cut with a steel tool in a hand-operated dividing engine with a reading limit of 0·001 mm. It is therefore too much to expect the above limit of accuracy, but it has been found possible to cut by hand to 0·0025 mm. For the cutting, a tool about

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0·120 mm. in width is used to make the edge-cuts in each strip, as the smaller resistance encountered in this part of the work allows of gentler handling. A grating can be cut in about three hours.

As an example of the accuracy obtainable with the apparatus, the second platinum set of gratings may be instanced. Each of the four gratings was measured with a microscope whose reading limit was 0·001 mm. The average error in each of the sets of strips varied between 2·5 and 3·5 thousandths. Table 1 shows a number of consecutive readings of b and c for the grating B. The unit is 0·001 mm.

Table 1

| b | 484 | 487 | 489 | 492 | 485 | 491 | 492 | 490 | |
| c | 512 | 513 | 512 | 512 | 512 | 515 | 509 | 511 | 511 |

When it has been measured the set of gratings is prepared for use by grinding the back to prevent internal reflection, and painting with photographic black on back and sides and unwanted parts of the front. Care must be taken to include equal numbers of glass and metal strips in each set.

§ 4. EXPERIMENTAL ARRANGEMENTS FOR OBTAINING DIFFRACTION SPECTRA

The finished grating is mounted on the table of a prism spectrometer fitted with a quarter-plate camera, and is supported against a vertical wooden block. A stop having an aperture of width equal to the length of a strip is used to block off the light from all gratings except the one from which photographs are being taken. The aperture of the stop is at a fixed height (the centre of the collimating lens), so that the grating plate must be raised or lowered to bring into use the different sets of strips. It is important that the whole of a set comprising a grating should be within the collimated beam so that a definite integral number of strips may be in use. A mercury arch is used as a source in view of its convenient line spectrum. The experimental arrangement is shown in figure 4.
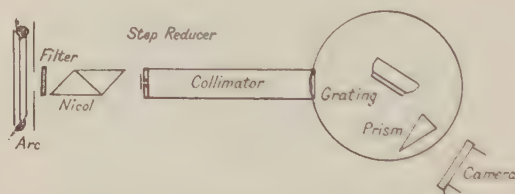
Figure 4. Experimental arrangement for obtaining diffraction spectra.

The reflected and diffracted beam passes through a 30° glass prism set approximately at minimum deviation for the yellow lines. This serves to disperse the beam into its components, each line being accompanied by its diffracted images. The slit is made fine enough to resolve the yellow lines. A reproduction of a typical spectrum is given, in figure 5, the electric vector being parallel to the plane of incidence.

The polarizing nicol is placed immediately before the slit, the direction of the electric vector being determined by setting the shorter axis horizontally or vertically. The polarization of the incident beam is tested by observing the images through another nicol and ensuring that complete extinction can be obtained.

Figure 5. Typical spectrum in which the electric vector is parallel to the incident plane.
r, central reflected image; d, principal diffracted image.
The second principal diffracted image is missing.

The incident angle must be known accurately. With the prism and spectrometer which were used the range available was limited. It was desirable that it should be at least 65° or else α_p was so small that β/α became large and inaccurate. However, it was more important that none of the images should overlap. In order to keep separate the green and yellow groups it was found that the incident angle should be less than 70°. Unfortunately there was also trouble in the violet where the 4078 Å. line almost coincided with the first diffracted image of $\lambda 4046$, the effect being appreciable in the case of E_s only. Angles of 66°–69° were most satisfactory.

When a convenient angle has been found the camera is adjusted so that the central image of the blue line, $\lambda 4358$, coincides with a reference line on the back of the camera, and is then locked in position. Any slight alteration in incident angle made when the gratings are moved can then be detected and corrected by turning the table so that the images are always in the same place with reference to the back of the camera.

§ 5. MEASUREMENT OF INTENSITY RATIOS

In accordance with the usual custom of those engaged in the measurement of relative intensities in the optical region of the spectrum a photographic method was employed for determining the ratios. The plates were calibrated to find their characteristic density exposure curve and were examined with a Moll microphotometer.

It will be apparent from later consideration of the accuracy obtainable with the method that the factor of greatest importance is the exact measurement of the intensity ratios. It is hoped that these quantities may be determined with a probable error, of one part in two hundred. Investigators using the methods of photographic photometry have not attained this degree of accuracy, limiting their claims to two or three per cent, whilst recently the view has been expressed that about ten per cent is the best that can be hoped for. However, this problem is not identical with those generally attacked, in that lines of the same wave-length are being compared, and so no allowance need be made for the variation in sensitivity of the plate with wavelength. This increases the range of methods available for providing for the calibration of each plate.

For various reasons it was decided to use an optical wedge for the purpose of calibration. The principle of the method is to expose the plate for a suitable time to a beam of uniform, monochromatic, and parallel light falling normally on to the wedge which is placed immediately before the plate. There is then obtained a strip of suitable dimensions, the density of which varies in a manner characteristic of the plate and for which the exposure at any point is a function of the constants of the wedge and of the distance from an arbitrary zero.

d, I_0, I_1 The optical density d of an absorbing film is defined by the relationship $d = \log_{10}(I_0/I_1)$, where I_0 and I_1 are the intensities of the incident and transmitted beams, respectively. The wedge, which is 10 cm. in length, is designed to give a linear increase of density from 0 to 3. Hence the ratio of the transmitted beams at any two points distant x cm. apart, I_0 being the same for both, will be $I_1 I_2$,

x

k which $= 10^{kx}$. The value of k, which was not verified, was given as 0.31 cm.$^{-1}$

Calibration by means of a wedge depends on certain assumptions as to the behaviour of a photographic plate. The optical density of the image produced on a plate by exposure to monochromatic light depends on many factors and is usually assumed to bear a relationship expressible mathematically as,

$$d = \log f(I, t, \lambda, \text{conditions of development temperature of}$$
$$\text{exposure, age and brand of plate, etc.}),$$

I, t, λ where I is the intensity, t the time of exposure, and λ the wave-length. For images on one plate we may put

K, s
$$d = \log(KI^s t^p), \qquad K \text{ being a constant,}$$
$$= s \log I + p \log t + \log K,$$

p where p is Schwartzchild's constant.
d_1, d_2 Now suppose there are two images to be compared having densities d_1 and d_2
I_1, I_2 due to intensities I_1 and I_2 and an exposure time t. These densities are measured and the straight portion of a characteristic curve is used to find their equivalence to two
I', t' intensities I' and kI' and an exposure time t' (λ being the same and the curve being taken from a strip on the same plate). Then

$$d_1 = s \log I_1 + p \log t + \log K,$$
and
$$d_2 = s \log I_2 + p \log t + \log K,$$
so that
$$d_1 - d_2 = s \log(I_1/I_2).$$
And we have found that
$$d_1 = s \log I' + p \log t' + \log K,$$
and
$$d_2 = s \log kI' + p \log t' + \log K,$$
so that also,
$$d_1 - d_2 = s \log k^{-1}.$$
Therefore
$$I_1/I_2 = k^{-1}.$$

The variation in d caused by the differences in times of exposure and intensity of illumination is thus eliminated. Of course we have not assumed that the reciprocity

law holds (i.e. that $p = s$), but only that p and s do not change rapidly with I and t. Exposure times for images and calibration strips are therefore made comparable.

All photometry is done with the Moll microphotometer. Instead of optical density, percentage transmission is measured, and the curves are plotted on a logarithmic scale to give the same result as a density curve on a linear scale. The calibration strips are measured by hand-operation of the photometer. Starting from an arbitrary zero, at each millimetre along the strips readings are taken of the galvanometer deflections due to light passing through the exposed strip and through the unexposed portion adjacent. The ratio of these is plotted against the distance from the zero and a characteristic curve thus found. Each deflection can be read on the scale to 0·1 mm. representing about 0·2 per cent variation in transmission.

Photographic records are used in the case of the lines. No allowance need be made for continuous background, as none can be found even in the heaviest exposures, and so the usually flat base provides a means for easily estimating the deflection through the unexposed portion of the plate.

Since the intensity scale in the calibration curve is logarithmic (mm. of wedge), the percentage transmission for each of two lines whose ratio is to be measured will be equivalent to a certain distance, expressed in millimetres. The difference of these will be a distance, expressed in tenths of a millimetre, which multiplied by the wedge constant and converted to the antilogarithm will give the ratio of the intensities. This procedure is illustrated in table 2.

Table 2. Method of measuring intensity ratios. Plate 1. λ 4046. Grating B. E_p

Diffracted images				Central image		Wedge	Reducer
Per-centage Right	Trans-mission Left	Mean	Wedge (mm.)	Per-centage trans-mission	Wedge (mm.)	Differ-ence (mm.)	Wedge differ-ence (mm.)
D 17·8	17·6	17·7	16·6	69·5	33·6	17·0	16·8
L 69·4	67·7	68·6	33·4	—	—	15·2	
D 19·3	17·9	18·6	17·2	62·6	31·9	14·7	15·4
L 68·3	63·5	65·9	32·6	—	—	14·3	
D 19·5	21·1	20·3	18·2	65·8	32·6	14·4	14·8
L 66·5	67·5	67·0	33·0	—	—	14·6	
D —	—	—	—	35·6	24·4	15·4	15·3
L 33·2	35·0	34·1	24·0	87·0	39·2	15·7	
D 20·0	20·3	20·2	18·1	72·4	34·4	16·3	15·3
L 69·5	68·3	68·9	33·4	—	—	16·0	
D 44·1	42·3	43·2	26·6	88·2	40·5	13·9	—

Mean 15·2
Mean error = 0·8 mm.

Ratio I_1/I_0 = antilog (15·2 × 0·031)
      = 2·98.
Ratio I_0/I_1 = 0·336.   Probable error = 1·5 %.

The first and second columns give the percentage transmissions for each of the two diffraction images to right and left of the central image. The fourth and sixth columns give the abscissae on the calibration curve corresponding to the percentage transmissions. These figures depend on the arbitrary zero chosen. The seventh column is the difference between the fourth and sixth and is a measure of the ratio.

Six photographs have been taken at this particular ratio and in addition a step reducer has been used to divide the image on the plate into two halves of different densities, each of which, in the case of the diffraction maxima, was suitable for measurement*. The double sets of figures in the first two columns thus give the percentage transmissions for the more dense (D), and less dense (L), portions of the line on the plate. By using a mean value of $15 \cdot 0$ mm. for the factor of the reducer two values of R are obtained from each photograph.

In this case the central image was weaker than the diffracted images, giving rise to larger percentage transmissions and larger wedge distances. Hence the ratio expressed in the seventh column is I_1/I_0.

In the last column are given values for the reducer factor which are the differences between the two sets of figures given in column four.

The probable error is calculated from the mean error by dividing by the square root of the number of observations. It can immediately be expressed as a percentage error.

A large amount of material had to be accommodated on each plate, and because of the little space required the wedge method was the most convenient. If three gratings are used six photographs must be taken, since it is desirable that both polarizations should be included on one plate. A single determination of an intensity ratio is not, however, of much value, the best way of ensuring accuracy being to average as many values as possible. By using both horizontal and vertical movements of the plate in its holder it was found possible to accommodate thirty-six photographs of spectra, each 20 mm. by 3 mm., thus providing for six measures of each ratio, although other considerations limited this number to four. Space was left in the centre of the plate for four calibration strips 2 mm. wide and 2 mm. apart, extending over the length of the plate.

A simple monochromator with mercury arc as source was used for the calibration exposures. In front of the plate, at a distance of 180 cm. from the slit, were placed the wedge and a screen having in it a slit 2 mm. wide and 9 cm. long, which was moved over the face of the plate to expose the four strips. The instrument was made quite light-tight so that plates might be handled freely without fear of fog. The necessary exposure times varied from one minute for the blue to six minutes for the yellow.

Owing to the limited range of density which can be measured with a Moll microphotometer, great care was necessary in the photography of the spectra. If

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* The step reducer consisted of a piece of photographic plate 5 mm. wide and 12 mm. long. The film was removed from half its length and it was placed directly before the slit so that one half of the latter was illuminated by light passing through the clear glass and the other half by light passing through the slightly opaque film.

a Wratten K1 filter is used the yellow and violet groups are of about equal effective intensity as also are the blue and green, but the latter are about three times as strong. In the case of E_p the ratios are small and a direct comparison is possible so that the use of a 3 : 1 step reducer enables the simultaneous photography of all four sets at suitable densities. When E is perpendicular to the incident plane the ratios are much larger and a different reducer is required. This necessitates separate exposures for the two groups of lines, those for the yellow and violet being much longer. Hence twice as many photographs must be taken in this case and only four measures of each ratio may be made.

It has been assumed that the characteristics taken from the centre of the plate may be used for photographs near the edges. This means that perfectly uniform development is necessary. At first a flat dish was used, but all plates from which results have been taken have been developed in a modified form of the tank described by Dobson, Griffith, and Harrison*. In this method there is a violent stirring of the developer over the face of the plate and the action is hastened, half the usual time being sufficient.

§ 6. RESULTS OBTAINED WITH PLATINUM GRATINGS

The preliminary trials made with silver gratings and sodium light were unsatisfactory and served only to show that because of its very high extinction coefficient silver was not a suitable metal for use in developing accuracy in the method. Platinum was found to be most convenient and the results obtained with two platinum gratings will be presented very briefly.

The first platinum grating was prepared by sputtering in vacuo for five and a half hours at a pressure of about 0·1 mm. with an unrectified a.c. electrode current of 20 mA. It was nearly opaque and showed no selective transmission. The refractive index of the glass was found to be 1·52 for sodium light, and tables were used to find the values of n at other wave-lengths. The dimensions of the grating were:

Grating	A (mm.)	B (mm.) .	C (mm.)
b (glass)	0·501	0·671	0·840
c (metal)	0·499	0·329	0·160

Three plates were taken from this set of gratings. For the first the intensity ratios will be given, and for the others the final results only.

The figures in table 3 show a regular change of R with wave-length and grating. A change in the optical properties would also seem to be indicated, but, as will be seen from the following tables, the wave-length variation is chiefly due to the slowly varying phase differences. The low values of R in table 3 (a) for grating B are remarkable. The substitution of the figures in the formulae given on page 51 results in the series of mean values of β/α and $\cos \delta$ given in table 4.

* *Photographic Photometry*, p. 77.

Table 3. Plate 1. Intensity ratios I_0/I_1

(a) Electric vector parallel to the plane of incidence, E_p.

Line (Å.)	Grating A	Probable error (%)	Grating B	Probable error (%)	Grating C	Probable error (%)
4046	0·77	1·0	0·336	1·5	0·565	0·8
4358	0·71	1·4	0·238	2·5	0·518	1·5
5460	0·725	0·7	0·262	—	0·472	2·0
5769	0·765	1·2	0·304	2·0	0·598	2·0
5789	0·805	1·0	0·313	3·0	0·586	1·0

(b) Electric vector perpendicular to the plane of incidence, E_s.

Line (Å.)	Grating A	Probable error (%)	Grating B	Probable error (%)	Grating C	Probable error (%)
4046	2·11	2·0	2·77	2·0	7·66	2·5
4358	2·96	1·0	4·00	1·5	12·65	1·0
5460	4·37	0·5	6·09	3·0	18·0	—
5769	4·54	1·5	5·68	—	15·9*	1·0
5789	4·30	0·3	5·78	2·5	15·9*	1·0

* Combined results.

Table 4. Plate 1. β and δ

Line (Å.)	E parallel to plane of incidence				E perpendicular to plane of incidence			
	β/α	β	$\cos \delta$	δ	β/α	β	$\cos \delta$	δ
		%				%		
4046	3·02	40·3	− 0·730	136° 53′	1·66	85·1	− 0·024	91° 23′
4358	2·95	39·9	− 0·878	151° 24′	1·35	68·8	0·116	83° 20′
5460	3·04	41·4	− 0·874	150° 56′	1·35	68·1	0·332	71° 13′
5769	3·01	41·0	− 0·835	146° 37′	1·55	78·8	0·349	69° 54′
5789	3·09	42·0	− 0·832	146° 18′	1·49	75·3	0·310	76° 56′

With the formulae $\beta_p/\beta_s = \tan \psi$, and $180° - \delta_p - \delta_s = \Delta$, the values in table 5 are found for the optical constants. The incident angle was 66° 30′.

Table 5. Plate 1. Optical constants

Line (Å.)	ψ	Δ	k	n	nk
4046	25° 19′	225° 30′	1·12	2·89	3·24
4358	30° 4′	249° 4′	1·61	1·55	2·49
5460	31° 18′	259° 43′	1·90	1·15	2·19
5769	27° 42′	256° 43′	1·33	1·48	1·97
5789	29° 10′	254° 22′	1·49	1·44	2·15

Some time later two plates were taken under the same conditions with an incident angle of 69° 6′. The focusing at the violet end of the spectrum was at fault in both plates and the intensity ratios differed materially from those quoted. The summarized results are given in tables 6 and 7.

Table 6. β and δ for plates 2 and 3

(a) Plate 2.

Line (Å.)	E parallel to plane of incidence				E perpendicular to plane of incidence			
	β/α	β	cos δ	δ	β/α	β	cos δ	δ
		%				%		
4046	2·58	48·3	− 0·720	136° 9′	1·70	93·0	0·020	88° 50′
4358	2·46	46·2	− 0·798	142° 56′	1·51	80·4	0·212	77° 45′
5460	2·53	48·0	− 0·787	141° 54′	—	—	—	—
5769	2·63	49·8	− 0·746	138° 15′	1·83	95·6	0·392	66° 55′
5789	2·60	49·2	− 0·756	139° 6′	1·81	94·8	0·412	65° 40′

(b) Plate 3.

Line (Å.)	β/α	β	cos δ	δ	β/α	β	cos δ	δ
4046	2·63	49·2	0·715	135° 38′	1·48	81·1	− 0·113	96° 29′
4358	2·54	47·7	− 0·730	136° 53′	1·70	90·4	0·071	85° 54′
5460	2·62	49·6	· 0·754	138° 56′	1·68	88·0	0·375	67° 58′
5769	2·58	48·8	− 0·775	140° 48′	1·73	90·4	0·402	66° 18′
5789	2·64	50·1	− 0·749	138° 30′	1·74	91·1	0·438	63° 0′

Table 7. Optical constants from plates 2 and 3

(a) Plate 2.

Line (Å.)	ψ	Δ	k	n	nk
4046	27° 23′	227° 13′	1·32	3·18	4·20
4358	29° 54′	245° 9′	1·61	1·57	2·53
5769	27° 34′	251° 20′	1·34	1·88	2·52
5789	27° 24′	253° 26′	1·33	1·83	2·44

(b) Plate 3.

Line (Å.)	ψ	Δ	k	n	nk
4046*	31° 15′	219° 19′	1·79	3·60	6·45
4358	27° 48′	231° 0′	1·37	3·65	5·00
5460	29° 56′	250° 8′	1·56	1·77	2·76
5769	28° 22′	254° 30′	1·42	1·72	2·44
5789	28° 46′	254° 30′	1·47	1·69	2·48

* β_s was calculated with A and B gratings only.

Discussion. The values of k and n are of the right order and are sufficiently close to the accepted values to offer strong support to both the theoretical explanation and the principles of the experimental method. However, the accuracy of these figures is such that little weight can be placed on the individual values of k and n, the erratic variation of the constants with change of wave-length showing weakness in this direction.

It seems desirable to use three gratings and to combine the results in pairs to obtain for β a value of any worth. The mean values of β were generally accurate to within about 1 per cent. As examples of the consistency which can be obtained two of the better cases are quoted.

These were by no means isolated cases as there were several other sets as good. The consistency of these figures gives confidence that no undesirable effects are masking the results predicted by the theory.

Combination	Plate 3, λ 5769, E_p		Plate 1, λ 5769, E_s	
	β/α	$\cos \delta$	β/α	$\cos \delta$
A–B	2·61	− 0·782	1·37	0·314
B–C	2·56	− 0·770	1·73	0·380
C–A	2·56	− 0·773	1·55	0·354
Means	2·58	− 0·775	1·59	0·349

Six values of k and n, each of reasonable worth, were obtained for the yellow lines. The mean values given in table 8 may be considered accurate to within 2 or 3 per cent.

Table 8. Optical constants for $\lambda\lambda$ 5789, 5769

Plate No.	Line (Å.)	ψ	Δ	k	n	nk
1	5789	29° 10′	254° 22′	1·49	1·44	2·15
2	5789	27° 54′	253° 26′	1·33	1·83	2·44
3	5789	28° 46′	254° 30′	1·47	1·69	2·48
1	5769	27° 42′	256° 43′	1·33	1·48	1·97
2	5769	27° 34′	251° 20′	1·34	1·88	2·52
3	5769	28° 22′	254° 30′	1·42	1·72	2·33
Means		28° 10′	254° 9′	1·40	1·67	2·33

The accepted constants for a sputtered film of platinum are $k = 2·10$, $n = 1·92$, and $nk = 4·04$[*]. The differences between the two sets of figures are greater than the estimated errors.

A second set of gratings was cut from a platinum mirror made by sputtering for one hour at 25 mA. with rectified A.C. The film was semi-opaque and definitely blue by transmitted light. Four gratings were cut, their dimensions being as shown in table 9.

Table 9

Grating	No. of strips	b glass (mm.)	c metal (mm.)	Mean error (mm.)
A	45	0·360	0·640	0·0028
B	40	0·489	0·511	0·0025
C	41	0·652	0·348	0·0035
D	39	0·770	0·230	0·0030

A contact print of this grating is given on a previous page, figure 3.

[*] *International Critical Tables*, 5.

When the grating was placed in position it was seen that the different thickness of the film had entirely altered all values of R. Those for E_s had increased enormously in a ratio of the order of $50 : 1$. As a result their measurement and the values of β and cos δ calculated from them were very inaccurate. Three plates were taken in about four hours but were calibrated separately. They showed disturbing variations in their characteristics and the resulting values of R for identical conditions differed greatly. The optical constants could only be deduced for $\lambda\lambda$ 5789 and 4046; they are given in table 10.

Table 10. Optical constants for $\lambda\lambda$ 5789, 4046

Line (Å.)	β_p (%)	β_s (%)	δ_p	δ_s	ψ	Δ	k	n	nk
5789	56·5	95·6	104° 39′	25° 11′	30° 33′	259° 28′	1·68	1·36	2·30
4046	45·0	74·6	94° 28′	30° 34′	31° 6′	243° 47′	1·76	1·81	3·19

These figures are of the right order and show a decreased reflecting power in the violet. Both values of δ are lessened owing to the thinner film, and the small value of δ_s is responsible for the very large values of R connected with that polarization.

§7. DISCUSSION OF METHOD

In the theoretical treatment several assumptions have been made which are not realized in practice.

The edges of the strips are not perfectly clean although a low-power microscope shows no irregularities greater than 0·001 mm., on the edges of a good cut. With a sharp tool and the correct angle on the cutting face there is no visible tearing of the metal. Under these conditions, too, the glass surface is not damaged, although with blunt tools and wrong methods it is possible to scratch and chip the glass.

The cleanliness of the surfaces is, of course, open to doubt since they cannot be touched after the grating has been cut. No tarnish is visible on a platinum mirror even after three months' exposure, and as sufficient photographs can be taken from a grating to determine the optical properties within six or eight hours after it has been constructed, any change due to exposure would seem to be negligible.

The fact that the metal and glass surfaces are not in the same plane has been ignored in the theoretical treatment. Assuming that the glass is perfectly flat and that the metal layer is of uniform thickness d, then the rays reflected from the glass surface travel farther than has been assumed, the extra path difference being $2d \sec \phi$, where ϕ is the angle of incidence, approximately 68°, so that $\sec \phi = 2\cdot8$. This is equivalent to a phase difference of $4\pi d \sec \phi/\lambda$ or $11\cdot2\, \pi d/\lambda$, and this is included in the values of δ_p and δ_s but not in Δ. With the value $k = 1\cdot5$ in the equation

$$I/I_0 = e - 4\pi k d/\lambda,$$

it is found that the thickness of the film is of the order of $0 \cdot 1 \lambda$, so that the phase difference introduced is about $180°$.

If the thickness of the metal is not uniform the phase difference will vary from place to place and for individual strips will have different values. The average value of cos δ which is obtained from the formula will not, however, be the cosine of the average of these phase differences and wrong values will result. It is therefore desirable that the film should be as uniform as possible. The shielding effect of the metal layer on the glass strip is negligible, since the width of the strip lost is about $0 \cdot 1$ per cent of the whole.

If the face of the glass on which the grating is ruled is not perfectly flat the angle of incidence will vary for different parts, and this variation will show itself in the images which will not, under these circumstances, focus sharply. Rough gratings made from thin plate which had been heated and cooled again showed this effect to a marked degree, but the 8-mm. plate glass used for the platinum mirrors gave perfectly sharp and clear images. The optical properties must be the same over the whole of the three or four gratings. For this reason a mirror was not used if there was any visible alteration in its reflecting properties or any blemish whatever on its surface. In addition, the region near the edges of the glass is avoided and only the central portion was used.

Since in the Drude method observations are made at only one angle of incidence, which in the case of platinum is about $78°$, any variation of k or n with the incident angle would not be apparent. However, as this method has been used with incident angles of about $68°$, the variation, if any, would not be large, and certainly less than that found.

The illuminating beam is assumed to be completely plane-polarized exactly parallel or normal to the incident plane. Any deviation from the correct setting of the nicol would be more serious in the case of E_p than with E_s, since α_p is about one-third of α_s. An error in this case will have the effect of increasing R by about 5 per cent per degree. In the other case R will be decreased but much more slowly since both α_p and β_p are small.

The many sources of possible error would seem to make accurate results difficult of achievement, but assuming that a grating can be constructed in which b and c shall be correct to within $0 \cdot 001$ mm. or less, the problem resolves itself into the exact measurement of R. The degree of precision desired, one part in two hundred, seemed rather ambitious, but was achieved in several cases. There is reason to hope that further refinement in the handling of plates and in calibration and photometry will reduce the errors in R.

The measurement of R is far more difficult when the ratios are greater than about eight to one, and it is interesting to see why high values may be expected. A glance at the formula for $\beta^2 \alpha^2$ gives the impression that β is determined chiefly by the *differences* in the various R's, and this view is supported by a detailed examination of the results. The magnitudes of the ratios depend chiefly on δ, as is apparent from the formula

$$R = \frac{\alpha^2 b^2 + \beta^2 c^2 + 2\alpha\beta bc \cos \delta}{A^2 (\alpha^2 + \beta^2 - 2\alpha\beta \cos \delta)}.$$

In the case of the second platinum grating the altered values of δ_s due to the thinner film caused large increases in the ratios. This is objectionable, and unless the variation of the optical properties with the thickness of the film is under consideration it will be desirable to increase the thickness, by visual trials with rough gratings, until the most favourable conditions are found.

On consideration of all errors which may be involved, it is thought not unreasonable to expect that β can be determined to within much less than 1 per cent. However, the use of the β's in the calculation of the optical constants reveals a weakness in the method which was very apparent in the case of silver. β_p/β_s gives us the tangent of an angle. This angle is doubled and its tangent is used to find k. For a given error in β_p/β_s, k will be most accurately determined when $\psi = 22 \cdot 5°$ and any small error in ψ will be greatly magnified when it approaches $45°$ as it does with silver. Consequently the method is limited in its application to metals having a value of ψ of about $22 \cdot 5°$. Platinum, chromium, antimony, steel, and copper come in this class, but, unfortunately, with only sputtering methods available, gratings may conveniently be made from only the first of these. Evaporation processes will enable the deposition of the other metals at a later date. When we deal with metals in this range ($\tan \psi = 0 \cdot 5$) the error in $\tan \psi$, of the order of 1 per cent, is multiplied by a factor of 4 or 5 in the calculation of k.

From the results it seems that Δ is not affected in the same degree by small errors. The effect on n when $\tan \psi = 0 \cdot 5$ and $\Delta = 250°$ or $260°$ is shown by the equation

$$dn = 5 \cdot 5 \, d \left(\beta_p / \beta_s \right) + 1 \cdot 4 \, d\Delta,$$

obtained by differentiating Drude's formula for n.

In the Drude method considerable time, perhaps several days, is required to find the most suitable conditions, especially in the case of a new metal or of one newly deposited. Observations must be made with monochromatic light and the constants are thus derived at different times, whilst in addition the visual work is rather laborious.

A grating may be cut by hand within three hours of a mirror surface having been prepared and, with an instrument already set up and preliminary photographs taken to find correct exposures, the effect can be examined immediately and two or three plates can be exposed within two hours. So that within six hours after the making of the mirror a permanent record of its optical properties can be made at several places throughout the visible and possibly even in the ultra-violet regions of the spectrum. Admittedly, the photometry and the calculation of the intensity ratios is laborious owing to the great amount of material on each plate, and the results can scarcely be worked out in less than a week, but the developed plate remains a permanent record.

Perhaps the greatest advantages of the method are the elimination of visual observation and the simultaneous measurement at several places in the spectrum, and it is hoped that further refinement will make the work sufficiently accurate to justify its wider use.

§ 8. ACKNOWLEDGMENTS

A FURTHER POINT OF ANALOGY BETWEEN THE EQUATIONS OF THE QUANTUM THEORY AND MAXWELL'S EQUATIONS

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ABSTRACT. A previous paper* dealt with an analogy between the electromagnetic equations in free space and the equations of the quantum theory, exhibited by means of five-dimensional geometry. In the present paper the analogy is pursued further and leads to the Eddington relation between the number of electrons in the universe and its radius.

———————

A SET of equations has been developed by Flint and Fisher in five-dimensional space by analogy with Maxwell's equations, as the fundamental equations of the quantum theory. They are written in the following form:

$$\frac{1}{\gamma^{\frac{1}{2}}} \frac{\partial}{\partial x^{\nu}} (\gamma^{\frac{1}{2}} A^{\mu\nu}) - \frac{2\pi i}{h} \pi_{\nu} A^{\mu\nu} = 0 \qquad \qquad \ldots\ldots(1),$$

where μ and ν have the values 1, 2, 3, 4, 5, $\pi_{\nu} = (P_{\alpha} + e\phi_{\alpha})$, where π_{α} is a momentum introduced by Prof. W. Wilson†, P_{α} is the component of the four-dimensional momentum, ϕ_{α} is the electromagnetic potential and $A^{\mu\nu}$ is an antisymmetric tensor of the second rank.

μ, ν, π_{α}
P_{α}
$\phi_{\alpha}, A^{\mu\nu}$

The author has previously shown in a communication to the Physical Society*, hereinafter called "the first paper," that the components of the tensor $A^{\mu\nu}$, except A^{m5}, are related in a simple way to the magnetic and electric moments of a doublet. The A^{m5} are yet without a similar explanation.

Equation (1) may be written in the form:

$$\frac{\partial A^{mn}}{\partial x^{n}} - \frac{2\pi ie}{h} \phi_{n} A^{mn} - \frac{2\pi ie}{h} \phi_{m} \psi_{0} + \frac{2\pi i}{h} mc A^{m5} + \frac{\partial \psi_{0}}{\partial x^{m}} = 0 \quad \ldots\ldots(2),$$

where m and n have the values 1, 2, 3, 4‡.

m, n

To make equations (2) identical with those developed by Dirac and others, the condition $A^{n4} = iA^{n5}$ ($n = 1, 2, 3$) was imposed, together with other conditions, with which we are not here concerned.

In a further paper§ the author has shown that the tensor A can be given a geometrical significance in agreement with a suggestion in Flint and Fisher's paper. It is then to be expected that it will have a cosmical significance. This significance has been expressed precisely by Sir Arthur Eddington‖, and from his paper we can

* *Proc. Phys. Soc.* **43**, 124 (1931).
† *Proc. R. S. A,* **102**, 478 (1923).
‡ *Proc. R. S. A,* **126**, 644 (1930).
§ *Proc. Phys. Soc.* **44**, 368 (1932).
‖ *Proc. R. S. A,* **133**, 605 (1932).

deduce the actual value of A^{45}. In the present paper we deduce this value and from the results of the first paper we deduce A^{15}, A^{25} and A^{35}.

By applying the result of Flint and Fisher, $A^{n4} = iA^{n5}$ $(n = 1, 2, 3)$, we can then deduce Eddington's value of the radius of curvature of the universe.

This result is now more than a mere identity. The identification was demanded in order to simplify a general result and bring it into line with known equations, but clearly the relation should be more than an identity. The failure to give a new result rested on the fact that A^{m5} could not be identified cosmologically. Eddington's result supplies the meaning of these components and then the relation gives a link between the cosmological R and the atomic e and m—a relation between one of the largest and some of the smallest quantities in physics.

Putting m equal to 4 in equation (3) we get:

$$\frac{\partial A^{4n}}{\partial x^n} - \frac{2\pi i e}{h} \phi_n A^{4n} - \frac{2\pi i e}{h} \phi_4 \psi_0 + \frac{4\pi i}{h} mc A^{45} + \frac{\partial \psi_0}{\partial x^4} = 0$$

or
$$\frac{\partial A^{41}}{\partial x^1} + \frac{\partial A^{42}}{\partial x^2} + \frac{\partial A^{43}}{\partial x^3} + \frac{1}{ic} \frac{\partial \psi_0}{\partial t} - \frac{2\pi i e}{h} \phi_4 \psi_0 - \frac{2\pi i}{h} mc A^{45} = 0 \quad \ldots\ldots(3).$$

Eddington gave the equation for an electron in the electrostatic field due to a fixed electron in the following form:

$$\left\{ i \left(\alpha \cdot \frac{\partial}{c\partial t} + \frac{i}{r} \right) + i_{14} \, x \cdot \frac{\partial}{\partial x} + i_{21} \, x \cdot \frac{\partial}{\partial y} + i_{34} \, x \cdot \frac{\partial}{\partial z} \right\} \psi_1 + \left\{ i_4 \left(\frac{i}{R} \right) \right\} \psi_0 = 0 \quad \ldots(4).$$

where $\psi_n = n^{\frac{1}{2}} \psi_1$, n is the number of electrons in the universe, R the radius of curvature of the universe in a static state, and

α
$$\alpha = \frac{hc}{2\pi e^2} \quad \ldots\ldots(5).$$

Equations (3) and (4) are so alike in form that in spite of the difference of notation we may compare them and so we obtain the following relations:

$$A^{45} = \frac{h}{2\pi mc R} \psi_n; \quad \frac{\psi_0}{\psi_1} = -\alpha \quad \ldots\ldots(6).$$

Thus
$$A^{45} = -\frac{h}{2\pi mc\alpha} \frac{n^{\frac{1}{2}}}{R} \psi_0$$

$$= -\frac{e^2}{mc^2} \frac{n^{\frac{1}{2}}}{R} \psi_0 \quad \ldots\ldots(7).$$

This relation gives a new meaning to the component A^{45} and shows the cosmological character of the component. If we make use of the fact that the ratio between A^{n5} and A^{45}, where $n = 1, 2, 3$, is

$$\frac{4\pi m}{he} \frac{N_n}{i},$$

N_n where N_n is the component of the electric doublet, we have as the value of A^{15}, for example,

$$A^{15} = i \frac{4\pi c N_1}{hc^2} \frac{n^{\frac{1}{2}}}{R} \psi_0 \quad \ldots\ldots(8).$$

There are of course similar values for A^{25} and A^{35} and the cosmological character of the components containing the suffix 5 is brought out.

By the relation $A^{n4} = iA^{n5}$ of which a particular case is

$$iA^{15} = A^{14},$$

we have, since

$$A^{14} = -\frac{4\pi m}{he} N_1 \psi_0,$$

by the table of the first paper

$$\frac{n^{\frac{1}{2}}}{R} = \frac{mc^2}{e^2} \qquad \qquad \ldots\ldots(9).$$

It is very surprising to find how the relations of Flint and Fisher's paper, which are demanded by the first-order equations of the quantum theory, fit into widely different applications of those equations, e.g. in the derivation of Maxwell's equations* and again here in the determination of the cosmical constant λ, the actual value of λ being derived† immediately from equation (9) since $\lambda = R^{-2}$.

In conclusion I wish to thank Dr H. T. Flint for his advice and help in the above work.

* *Proc. Phys. Soc.* **43**, 368 (1932). † *Proc. R. S. A*, **133**, 613 (1932).

55.083.4   552.122:539.32

ON THE ELASTIC CONSTANTS OF ROCKS, WITH A SEISMIC APPLICATION

By T. C. RICHARDS, A.R.C.S., B.Sc., D.I.C.

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ABSTRACT. The results of a geophysical survey by means of the seismic method over a large oil-bearing limestone structure in south-west Persia indicate that the limestone possesses a higher elastic velocity at its lower boundary than at its upper. Specimens of the limestone at different depths obtained by coring do not give the same elastic constants when measured by a simple optical method, and the bearing of this result on the practical seismic observation is discussed.

§ 1. INTRODUCTION

THE application of the seismic method in geophysical prospecting for buried structures is entirely dependent on the difference between the elastic properties of the structure sought and those of the overburden. The determining property is the velocity of the elastic waves, and by suitable observations with seismographs and the subsequent drawing of distance time curves, it is possible to detect the presence of some high-velocity medium and to determine its depth. If the velocities of both longitudinal and transverse waves through any medium be known, then the medium may be defined in terms of the usual elastic constants, E and σ, and conversely.

E, σ

In this paper the constants E and σ for representative specimens of cap rock and an oil-bearing limestone in south-west Persia are determined in the laboratory and the calculated wave velocities are compared with those indicated on distance time curves, obtained by observations with the Jones vertical seismograph.

§ 2. METHOD AND PREPARATION OF SPECIMENS

The principle of the method depends on the bending of a rectangular plate, by means of terminal couples, into an anticlastic form.

The rectangular plates were cut from rock samples obtained by coring, the cores being, of necessity, limited in size. Little difficulty was experienced in selecting a good sample of cap rock, but in the case of the oil-bearing limestone it was important that the samples should be free from fissures. As an optical interference method was proposed for measuring the surface deformations after bending, it was then necessary to polish one face of each plate as far as practicable to optical flatness. It was impossible to obtain perfect optical flatness, the non-cohesive and granular qualities of the specimens as compared with a substance such as glass being deterrents in this respect. Messrs C. Baker and Sons were successful in polishing the faces to a degree which made the application of the method possible.

Incidentally, although the limestone specimens were obtained from the same bed, each had to be polished individually, owing to the existence of slight differences in hardness. The dimensions of the plates, which were governed by such factors as the size of the original core and the cutting and polishing processes, were approximately 10 × 5 × 0·5 cm.

§ 3. THE APPARATUS

The bending apparatus, figure 1, is of simple design. The steel knife edges are adjustable so that the applied couple may be varied either by means of the couple
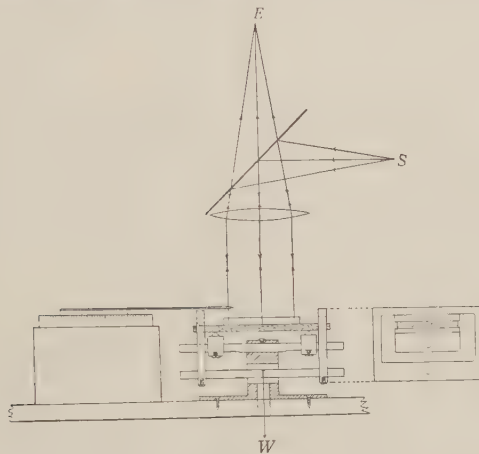

Figure 1.

arm or the applied load W, or both. In addition, by suitable disposition of the knife edges the couples can be reversed in sign. The optical system for producing and observing the interference fringes is self-explanatory from the figure. A sodium flame at S is sufficient for visual observations at E, where a magnified image of the interference pattern is seen. A needle and micrometer scale as shown to the left of the figure are sufficient to make the necessary measurements of the fringes.

§ 4. EXPERIMENTAL

The theory of the bending of a rectangular plate by means of terminal couples is given in the *Mathematical Theory of Elasticity* by A. E. H. Love, and leads to the expression

$$E = \frac{3G}{2bh^3 C_1} \cdot \frac{1 - \sigma^2}{1 + \sigma^2} \qquad \qquad \ldots\ldots(1),$$

where G is the applied couple,

b the width of the plate,

$2h$ the thickness of the plate,

C_1 the principal longitudinal curvature,

C_2 the principal transverse curvature, and

$\sigma = C_2/C_1$.

The principal curvatures are best found by determining the slopes of the straight lines representing the relation

$$C = 4\lambda n/d_n{}^2 \qquad \qquad ......(2),$$

n, d_n

where n is the number of the fringe measured from the centre and d_n is the distance between the vertices of the pair of the nth fringes.

In general, the unstrained surfaces of the rock specimens exhibited irregular interference patterns, and it became necessary, therefore, to apply couples of sufficient magnitude so that this original defect was masked in the resultant more or less regular pattern. Similar couples were applied to bend the plate in the opposite sense. The apparent principal curvatures were determined in each case, the arithmetical means giving the true curvatures.

Several determinations of the elastic constants were made for each specimen, the apparatus and test plate being reset for each. The values obtained both for E and for σ were fairly consistent throughout, the range of values being given in table 1. Crown glass was taken as a medium for comparison purposes. Tests were made on a long rectangular plate, from which the smaller plate had been cut, and the same range of values for E and σ were obtained.

Table 1

Material	ρ	E (c.g.s.u. $\times 10^{-11}$)	σ	Mean μ (c.g.s.u. $\times 10^{-11}$)	Mean K (c.g.s.u. $\times 10^{-11}$)	Mean V_L (km./sec.)	Mean V_T (km./sec.)
Crown glass	2·64	7·3–7·5	0·24–0·26	2·97	4·95	5·82	3·35
Cap rock	3·02	7·2–7·4	0·29–0·30	2·81	5·92	5·64	3·05
Limestone (19)	2·64	5·3–5·5	0·23	2·21	3·35	4·88	2·90
,, (158)	2·69	6·2–6·4	0·25–0·26	2·55	4·35	5·34	3·08
,, (215)	2·70	5·1–5·2	0·26	2·06	3·62	4·85	2·76
,, (596)	2·68	6·4	0·25	2·56	4·26	5·34	3·08
,, (702)	2·66	5·0–5·2	0·24–0·25	2·06	3·36	4·79	2·78

Cap rock is an impervious layer of anhydrite immediately overlying the limestone bed.

The values of the elastic constants of the limestone are such that no correlation between velocity and depth can be given; the physical properties of a single specimen taken from a particular depth cannot be regarded as typical for that depth throughout the limestone. The range of velocity values, however, is compared with those from seismic observations in table 3.

The values of E and σ for crown glass are in agreement with those published in tables of physical constants. The applied couples were approximately 10,000 gm.-cm. in each case, the mean couple arm being about 1·5 cm. The figures in parenthesis in the first column of table 1 denote the depth in feet into the limestone bed from which the specimens were obtained. The last two columns give the longitudinal and transverse velocities in accordance with the relations:

V_L

$$V_L = \sqrt{\left\{ \frac{E(1-\sigma)}{(1-2\sigma)(1+\sigma)\rho} \right\}} \qquad ......(3),$$

V_T

$$V_T = \sqrt{\left\{ \frac{E}{2(1+\sigma)\rho} \right\}} \qquad ......(4),$$
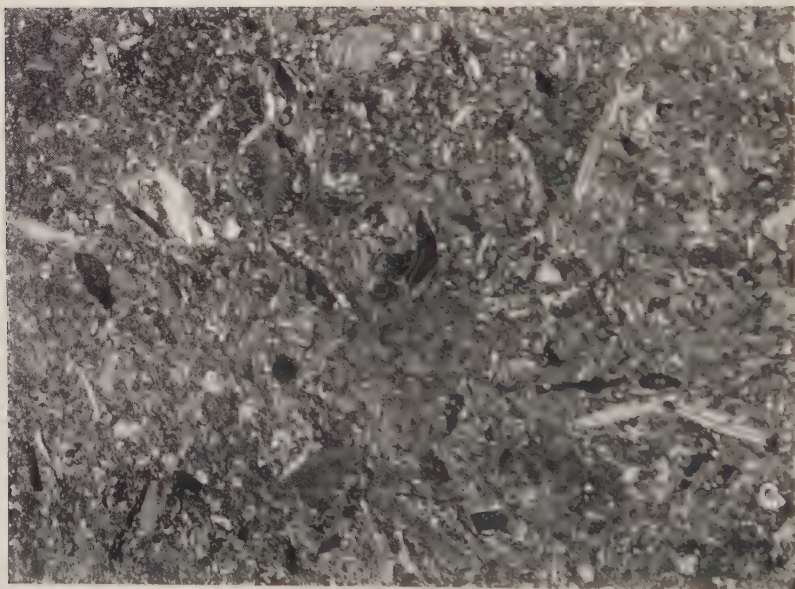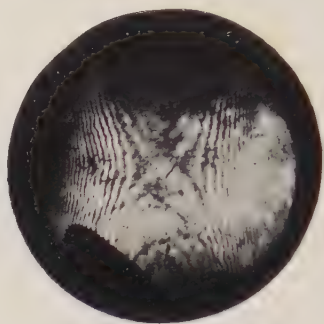
Figure 2.

ρ being the density. The calculated values for the rigidity μ and the bulk modulus K are also shown tabulated.

Photographs of the interference fringes for the two cases of bending of the cap-rock specimen are shown in figure 2; in addition figure 2 shows a photomicrograph of a limestone specimen, the fossiliferous nature of which is clearly marked.

§ 5. WAVE VELOCITIES FROM (DISTANCE, TIME) CURVES

Theory. Consider two media with elastic velocities V_0 and V, where $V_0 < V$, the inclination of the interface being α. The condition that a disturbance starting from O should travel along the path $OABP$, figure 3, in minimum time is that the

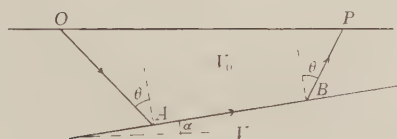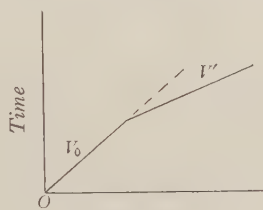

Figure 3.

Figure 4.

sine of the angle of incidence θ is equal to V_0/V. There is considerable experimental evidence from seismic observations at short distances from artificial earthquakes in support of this minimum time path, where a disturbance appears to travel along or close to the interface with the velocity appropriate to the second medium. A (distance, time) curve of the first elastic pulses arriving at a series of observation points, P, would appear as in figure 4. The slope of the first portion gives the true velocity in the first medium, and that of the second the apparent velocity in the second medium.

It is easy to show that

$$V' = V/(\cos \alpha - \cot \theta \sin \alpha) \qquad \ldots\ldots(5),$$

or, if observations are taken "down the structure,"

$$V' = V/(\cos \alpha + \cot \theta \sin \alpha) \qquad \ldots\ldots(6).$$

Equations (5) and (6) hold both for longitudinal and transverse waves, θ and V having the appropriate values.

From (3) and (4) we derive

$$\frac{V_T}{V_L} = \sqrt{\left\{\frac{1 - 2\sigma}{2(1 - \sigma)}\right\}} = \tau \qquad \ldots\ldots(7).$$

Poisson's ratio may also be defined as a function of C/V_T where C is the velocity of the Rayleigh wave. The satisfying equation* reduces to

$$x^3 - 8x^2 + 8x(2 - \sigma)/(1 - \sigma) - 8/(1 - \sigma) = 0 \qquad \ldots\ldots(8),$$

where

$$x = (C/V_T)^2.$$

* H. Jeffreys, *The Earth.*

Appropriate solutions of this equation for various values of σ are:

σ	0·5	0·4	0·3	0·25	0
C/V_T	0·95	0·94	0·93	0·92	0·87

The distance/time curves. A number of distance/time curves are shown in figures 5 to 9. These were obtained as a result of seismic observations over buried limestone structures in south-west Persia. The Jones vertical seismograph was used throughout. The letters L, T and R denote the arrivals of the longitudinal, transverse and Rayleigh waves.

Longitudinal arrivals. The identification of the first two or three longitudinal arrivals is not difficult; it is generally possible to detect the arrival of the wave which has followed an indirect path from the origin and that which has travelled close to the surface of the ground. In most cases the first high-velocity arrival vanishes rapidly with increasing distance, and this is possibly due to a damping effect caused by the oil- and gas-impregnated limestone or to the shattered rock surface which may exist in certain areas, or to both these causes. The second high-velocity arrival which persists for great distances has been attributed by Dr J. H. Jones, of the Anglo-Persian Oil Co., Ltd.*, to a deeper, more consolidated region of the limestone bed where the increase in elasticity more than compensates for the increase in density, if any.

Transverse and Rayleigh wave arrivals. Owing to the superposition of the coda of the longitudinal phase, the identification of the transverse arrival is very difficult. In the circumstances, the usual procedure is to choose a well-defined pulse and to follow it through on a series of seismograms taken at increasing distances from the origin.

The beginning of the Rayleigh phase is likewise masked by the coda of the transverse phase. A large pulse may, however, be followed through as for the transverse arrivals, figure 8. It may happen that the maximum amplitude of the Rayleigh phase is well marked, and figure 9 shows an example of the distance time curve in this case, the time being measured up to the point of maximum amplitude.

Each distance/time curve will now be considered in turn:

Figure 5 represents a strike traverse along the surface of a limestone outcrop. Two longitudinal velocities are recorded, namely, 15,360 and 18,500 ft. sec. The first velocity is that of the upper layers of the limestone while the second is attributed to a disturbance which has passed along the lower boundary*.
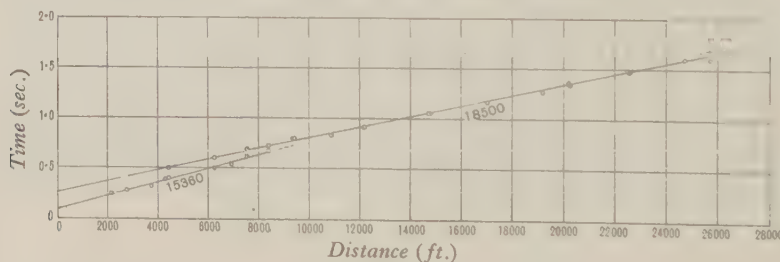

Figure 5.

* *Proc. R.S.* A, **137**, 341 (1932).

Figure 6 represents a strike traverse over the flank of a limestone anticline. The overburden consists of two definite media. The effective pitch of the structure is zero and thus 17,200 ft./sec. may be regarded as the true surface velocity of the limestone. The corresponding transverse velocity is 8900 ft./sec. The velocity of the longitudinal disturbance along the lower boundary of the limestone is 19,500 ft./sec.

Figure 6.

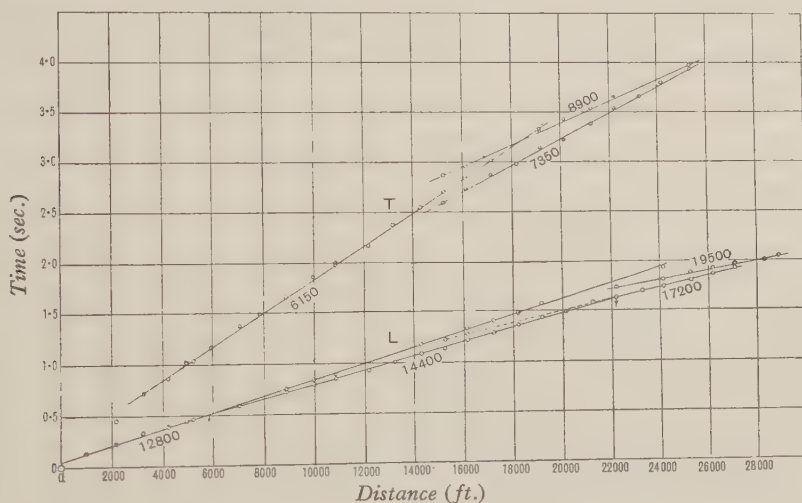Figure 7 represents an oblique traverse across an anticlinal structure. The overburden consists of two media. The limestone arrivals are indicated by the apparent velocities of 20,400 and 15,800 ft./sec. due to the rise and fall of the limestone, respectively, and by the true velocity of 17,600 ft./sec. obtained in the neighbourhood of the crestal region. The corresponding apparent transverse
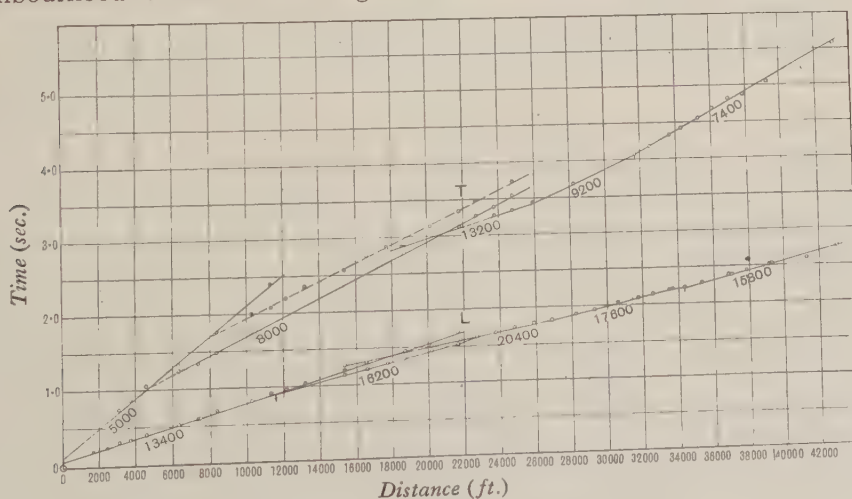

Figure 7.

velocities are 13,200 and 7400 ft./sec., and the true velocity 9200 ft. sec. This case affords an excellent illustration of the presence of an anticline, the position of the crest being easily determined from the time curve.

Figure 8 represents a strike traverse at the foot of a limestone outcrop. The traverse line was situated about 1000 ft. away from the commencement of the outcrop. The correspondence between the longitudinal velocities of 14,800 and 14,200 ft./sec. and the transverse velocities of 8200 and 7600 ft. sec., indicating the pitch of an upper bed, is well marked. The upper limestone velocities are 17,000
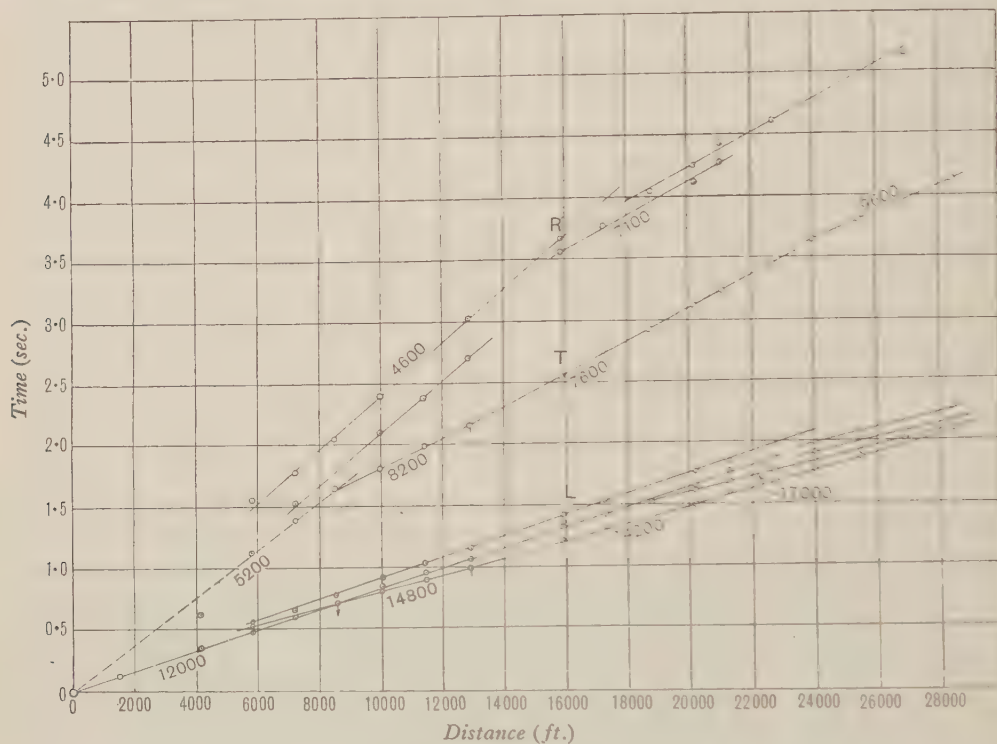
Figure 8.

and 9600 ft./sec., respectively. The short lines to the right of the diagram represent longitudinal high velocity arrivals from the lower regions of the limestone layer.

The attempt to trace the Rayleigh wave arrivals has led to practical confirmation of a theoretical aspect. The first portion of the curve gives the velocity of Rayleigh waves of short length in the upper medium, while the second portion is due to the longer waves which penetrate deeper and travel with the velocity of Rayleigh waves in the second medium if the first were considered absent. The Rayleigh velocity of 7100 ft./sec. corresponds to the transverse velocity of 7600 ft. sec.

Figure 9 represents a strike traverse over an anticlinal structure. There is no effective pitch and the velocities of 17,200 and 9200 ft. sec. may be regarded as true for the upper surface of the limestone. The longitudinal velocity along the

lower boundary of the limestone is 19,600 ft./sec. The maximum-amplitude arrivals in the Rayleigh phase are here plotted, and it is evident that the theoretical aspect alluded to above receives further support.
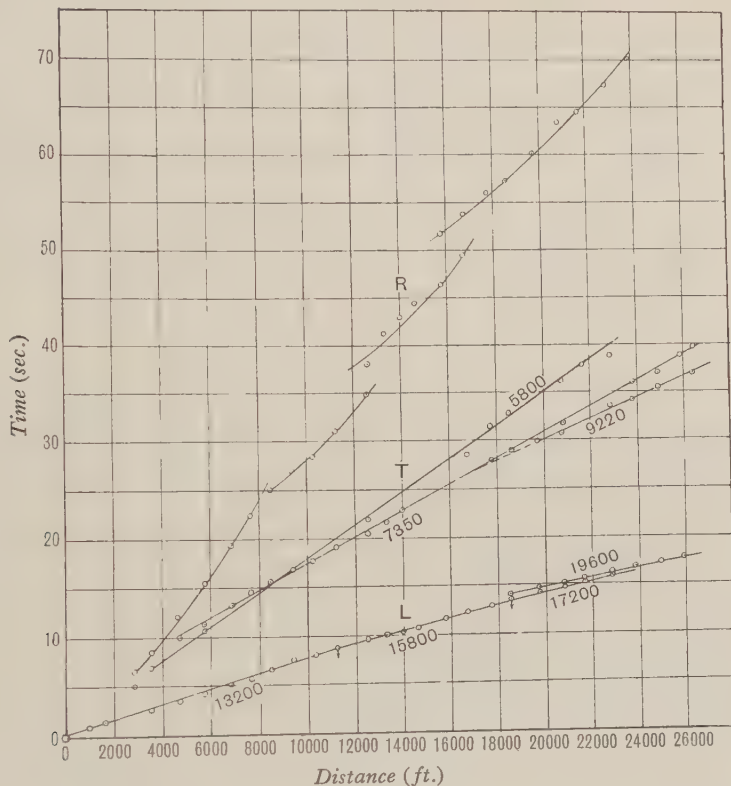
Figure 9.

The existence of a second high-transverse-velocity arrival, corresponding to the second high-longitudinal-velocity arrival from the lower boundary of the limestone, is difficult to detect.

Table 2 gives the elastic velocities and calculated constants. As a matter of

Table 2

Reference	V_L		V_T		σ	E (c.g.s.u. $\times 10^{-11}$)
	(ft./sec.)	(km./sec.)	(ft./sec.)	(km./sec.)		
Figure 5	15,360	4·68				
,, 5	18,500	5·64	8,900	2·71	0·31	5·15
,, 6	17,200	5·24				
,, 6	19,500	5·95	9,200	2·80	0·31	5·50
,, 7	17,600	5·36	9,600	2·92	0·26	5·76
,, 8	17,000	5·18	9,220	2·81	0·29	5·46
,, 9	17,200	5·24				
,, 9	19,600	5·97				

The longitudinal and transverse wave velocities and derived elastic constants σ and E from seismic observations over a buried limestone structure.

interest, the value of σ calculated by using the Rayleigh velocity in figure 8 and applying equation (8) is 0·33.

<div align="center">Table 3</div>

Method	Velocity range V_L (km./sec.)	Remarks
Laboratory	4·79–5·34	
Seismic observations	4·68–5·64	No overburden
	5·18–5·97	Overburden

<div align="center">Comparison between the limestone velocities as measured in the laboratory with those as given by seismic observation.</div>

§6. DISCUSSION OF RESULTS

As a result of extensive seismic surveys over an oil-producing limestone in south-western Persia, it has been established that the regions of greater oil productivity, necessitating greater fissuring, are associated with lower elastic velocities. These regions are situated in the upper layers of the limestone. It is of interest to note that in one part the upper layers are so compact, the oil-content being practically zero, that the longitudinal velocity is as large as 19,200 ft. sec. The velocity along the lower boundary of the limestone remains fairly constant, at nearly 20,000 ft. sec.

In the case of the seismic traverse over the limestone outcrop, figure 5, the upper and lower velocities are definitely both less than those found in cases where a thick overburden existed. The state of stress of the limestone seems, therefore, to be an additional factor governing the elastic velocity. It is interesting to realize that the pressure at an average depth of 3000 ft. to the limestone structure is about 1·5 ton/in.^{2}

The transverse velocities and the constants E and σ differ slightly from those obtained by the laboratory method. This may be attributed to the change in the physical conditions of measurement. The sensitiveness of σ to changes in V_T, V_L and C/V_T should, however, be noted. If we differentiate logarithmically equation (7), we obtain

$$\delta\sigma/\sigma = 3\delta\tau/\tau$$

in the neighbourhood of $\sigma = 0·25$.

The results of the laboratory method indicate that the limestone is not uniformly elastic. The low velocity of 15,800 ft. sec. compares favourably with that found by taking seismic observations on the limestone surface. It may be that if more samples were available and were tested in the laboratory, the high velocity of 17,500 ft. sec. would preponderate for specimens taken from the basal regions of the limestone bed.

With regard to the anhydrite, it is, no doubt, of insufficient thickness (0 to 150 ft.) to carry a detectable portion of the diffracted energy along its surface. The average thickness of the limestone is about 900 ft. The average length of a longitudinal

elastic wave, the frequency being taken as 15 to 20, is of the order of 1000 ft. Certain it is that no high velocity of 18,500 ft./sec. or more has ever been recorded on (distance, time) curves, where it would otherwise be expected as a result of the presence of anhydrite.

§ 7. CONCLUSIONS

The comparison of the elastic constants in the laboratory with those obtained by means of a seismic survey must have regard to the altered physical conditions of measurement. The chief of these is considered to be the state of stress enjoyed by the material. The non-uniformity of the limestone in its elastic properties is clearly demonstrated in the laboratory and helps to explain the two limestone velocities obtained by the seismic method.

§ 8. ACKNOWLEDGMENTS

DISCUSSION

Prof. A. O. RANKINE said that it was surprising that it had been found possible to form optical surfaces on the specimens sufficiently good for the purpose of the investigation. The author's idea had turned out to be an excellent one.

Dr J. P. ANDREWS. The method of flexure which the author employs is satisfactory only if certain precautions are taken. The best known of these is the separation of the inner knife-edges to a distance at least three times the width of the plate. A smaller separation, as in the present experiments, entails a reduction in the anticlastic curvature. It is equally necessary to keep the curvature as small as possible. Dr Ferguson and I published in 1928* an elaborate study of the flexure method; we showed there that only when the curvatures are very small is their ratio equal to Poisson's ratio as determined by the direct extensional method. The author was forced to employ larger curvatures. For both these reasons, therefore, his results for σ are too small, and his calculated values of V_1 and V_2 too large.

I should like to enquire whether any evidence of anisotropy in the specimens was found.

Experimental work on the variation of elastic constants at high pressures does not appear to be sufficiently complete to provide a comparison with the author's determination of velocities at different depths, but it might be pointed out that measurements by P. W. Bridgman on glass predict a decreased velocity for a transverse wave when the glass is under pressure.

* *Proc. Phys. Soc.* 41, 1 (1928).

Dr H. SHAW. This neat and interesting method appears to be well suited to hard rocks, though for obvious reasons it could not be applied to the softer rocks and strata.

Apparently in this investigation a couple of about 10,000 gm.-cm. was applied throughout, but I would like to ask the author if he has made observations under other applied couples, and if so whether any variations were obtained.

It is not clear whether the five limestone samples of table 1 were taken from the same core, or what amount of weathering or drying-out the specimens had undergone subsequently to their removal from the ground. Certainly no correlation can be given from the five results, but I think it is possible that if tests were made on a much larger number of specimens some connexion would be revealed between velocity and either the depth or the horizon. There appears to be ample evidence that the state of stress of the limestone is an important factor, while the degree of saturation should not be overlooked, and I would suggest that the author might consider making further tests, with his specimens—or perhaps the whole apparatus—immersed in oil under considerable pressure. In this way it might be possible to investigate the effect of varying depth under conditions approximating more closely to those of nature.

Dr J. H. JONES. The author states that it is difficult to detect the transverse-wave pulses corresponding to the high-velocity longitudinal pulses. On reference to figures 6 and 7 in the paper it appears to me that the transverse pulses plotted on these time curves correspond to the high-velocity longitudinal pulses and not to the upper boundary pulses with the lower velocity. Indeed it is doubtful if these latter pulses are shown in figure 7.

On the other hand, figure 9 suggests a transverse upper-boundary pulse, although the velocity is higher than that in figure 6. It is, I think, quite probable that there are two types of transverse pulses corresponding to the two longitudinal pulses, one travelling along the upper and the other along the lower boundary of the limestone.

AUTHOR'S reply. In reply to Dr Andrews: The conditions of the laboratory experiments admittedly did not rigidly fulfil the requirement of smallness of anticlastic curvatures or that for the separation of the inner knife-edges. My plates were the longest obtainable, and the width had to be sufficiently great to enable the somewhat irregular fringes to be examined over as large an area as possible. Actually the distance between the knife-edges was about $1\frac{1}{2}$ times the width of the plate. The lowering of Poisson's ratio on this account, judging by the work of Straubel quoted by Jessop*, would be of the order of 0·005, an amount which hardly affects the accuracy of measurement in the experiments. The greatest curvature into which any of the plates was bent was 0·25 $\times$ 10^{-3} cm.$^{-1}$, and here again I do not think the necessary correction to reduce the value of σ to that derived from very small curvatures would materially alter the working accuracy. If we assume an increase of 0·01 in σ, the transverse velocity is decreased by 1 per cent and the longitudinal velocity is increased by 4 per cent, values which approximately represent the

* *Phil. Mag.* **42** (1921).

accuracy to which we measure velocities from (distance, time) curves. No evidence of anisotropy was sought, as the experiments were mainly concerned with the velocities in directions parallel to the bedding plane and the plates were cut to fulfil this condition. The results of experiments by Bridgman are interesting, but are opposed to the seismic view for the longitudinal waves; the effect of pressure near the earth's surface tends to increase their velocity.

In reply to Dr Shaw: It was my intention at the outset to investigate the effect of varying the applied couple, but for small applied couples the fringes were too irregular for satisfactory measurements to be made. For large applied couples, of course, we tend more to violate the condition of smallness of curvature referred to above. The five limestone samples were all taken from the various cores from one well, and had been exposed to the air for six months or more. The degree of saturation is an important factor, and no doubt the variation in the calculated velocities is intimately connected with it.

I am inclined to agree with Dr Jones as to the probability of the existence of the lower-boundary transverse pulse but have not yet accumulated sufficient evidence from seismograms. In figure 6, if we take the two corresponding velocities as 19,500 ft./sec. and 8900 ft./sec., σ becomes 0·37, which is exceptionally high. With regard to figure 7, the calculated value for the dip of the structure is in good agreement with the actual dip, known from well data, when the velocities shown in the figure refer to the upper boundary pulses.

6

A COMMON MISAPPREHENSION OF THE THEORY OF INDUCED MAGNETISM

By L. R. WILBERFORCE, M.A., Lyon Jones Professor of Physics,
The University of Liverpool

ABSTRACT. It is usually stated that if any given magnet is immersed in a medium of permeability μ the magnetic field around it is similar to that in a vacuum, but diminished in strength in the ratio of $1 : \mu$. It is here shown that this statement is inconsistent with the ascertained experimental laws of induced magnetism.

I

H, K WHEN the process of magnetization by induction was first studied, attention was principally directed to the case of ideal media, such that at every point in them the magnetization I was collinear with the local magnetic force H and bore to it a ratio K, constant for that medium, and called its "magnetic susceptibility." (We shall, for the sake of brevity, employ electromagnetic units

B throughout.) In such ideal media the quantity called the "magnetic induction" B which in every substance is (in these units) the vector sum of H and $4\pi I$, is collinear with H and equal to the product of H and the constant factor $1 + 4\pi K$. This

μ factor is termed the permeability of the medium and is denoted by the symbol μ.

m If the magnetic field considered can be supposed to be due to a single pole of strength m completely surrounded by a vacuum, the value of H at a point distant

r r cm. from this pole will be m/r^2 and the direction of H will be radial. If the vacuum is now replaced by a medium of permeability μ, the strength of the pole remaining unaltered, H will be unchanged in direction but its magnitude will become $m/\mu r^2$.

It is commonly assumed to be a legitimate deduction from this result that if any given arrangement of constant magnets is surrounded by a vacuum and the

H_0 magnetic force at a given point external to the magnets is H_0, then if the vacuum is replaced by a medium of permeability μ the magnetic force at the given point will be unchanged in direction and become H_0/μ in magnitude. A closer examination of the problem will show that this deduction is in general fallacious.

It is well known* that the magnetic potential at any point in a magnetic field, whether internal or external to a magnet, is the sum of two integrals, the one involving surface distributions over the boundaries of magnets, and the other volume distributions within the magnets. At any point the density of this volume distribution is given by the expression

$$-\left(\frac{dA}{dx} + \frac{dB}{dy} + \frac{dC}{dz}\right),$$

* Clerk Maxwell, *Electricity and Magnetism*, **2**, 10.

where A, B, C are the rectangular components of I, and it is readily shown* that A, B, C wherever I is collinear with H and proportional to it this expression is zero.

Let us consider a magnet of any form with a constant but not necessarily uniform distribution of magnetization, and let it in the first instance be surrounded by a vacuum. Then let a portion of a substance with permeability μ or $(1 + 4\pi K)$ be introduced into its neighbourhood. The substance will become magnetized by induction and the value of H at any point, whether within it or not, will be changed, the new value being the resultant of the former value and a component due to the surface distribution over its boundary, since, as has been seen, the volume distribution in this case is zero. The density of the surface distribution will be the outward normal component of the superficial value of I in the medium, and I will be equal to KH where the value to be assigned to H is not that due to the magnet alone but to the magnet and surface distribution jointly.

If we now imagine the substance to expand until it completely displaces the vacuum, so that the surface of the substance coincides with the surface of the magnet, the same principles will still govern the calculation of the new value of H at any point.

When the magnet can be treated as a simple pole m of evanescent radius r_0, the r_0 calculation is easily made. Let the substance be in the first instance in the form of a spherical shell concentric with the pole and of inner radius r_1. At the inner r_1 surface of the shell, just within the medium, the value of H due to the pole will be $+ m/r_1^2$ and that due to the uniform surface distribution I will be $- 4\pi I$. The equation

$$I = KH$$

becomes

$$I = K \left(m/r_1^2 - 4\pi I \right)$$

and thus

$$I = \frac{K}{1 + 4\pi K} \times \frac{m}{r_1^2}.$$

Within the medium, at any distance r from the centre, the component of H due to the surface distribution is

$$- 4\pi . r_1^2 I/r^2 \quad \text{or} \quad - \frac{4\pi K}{1 + 4\pi K} . \frac{m}{r^2},$$

which may be written

$$(\mu^{-1} - 1) \, m/r^2,$$

and the result continues to hold good when the value of r_1 is diminished to r_0.

Thus the new value of H, the resultant of m/r^2 due to the pole and

$$(\mu^{-1} - 1) \, m/r^2$$

due to the surface distribution, is

$$m/\mu r^2.$$

The surface distribution over the outer surface of the shell does not affect the value of H inside the shell, even when the radius of this surface becomes infinitely great. Equally simple calculations on the same principle can be made if the magnet

* *Loc. cit.* p. 51.

L. R. *Wilberforce*

can be treated as a straight line with constant polarity per unit length or a plane with constant polarity per unit area, and in each case the value of H is found to be divided by μ when the medium is substituted.

If, however, the magnet occupies a finite volume this result will no longer be obtained. Let us consider, for example, the only case amenable to easy calculation, a sphere of radius a and uniform magnetization I. When such a sphere is surrounded by a vacuum the magnetic force at external points is the same as that due to a small magnet of moment $\frac{4}{3}\pi a^3 I$ at the centre of the sphere, with its axis in the direction of I, and at internal points the field is uniform and equal to $\frac{4}{3}\pi I$ in the direction opposite to I. The magnetization of such a sphere is equivalent to a surface distribution whose density at any point is $I\cos\theta$, where θ is the angle between the radius to that point and the direction of I.

If the vacuum is now replaced by a medium of susceptibility K, we can show that the density of the surface distribution over the boundary of this medium in contact with the sphere will be $-\alpha I\cos\theta$, where α is a constant calculable in terms of K, and hence that the magnetic force at any point external to the sphere is in this case unchanged in direction, but diminished in the ratio of $(1-\alpha):1$.

The proof is as follows. If we consider a point between the surface distribution due to the sphere and that due to the medium, the outward radial and θ-ward tangential magnetic forces due to the sphere will be

$$\tfrac{8}{3}\pi I\cos\theta \quad \text{and} \quad \tfrac{4}{3}\pi I\sin\theta,$$

and those due to the medium will be

$$\tfrac{4}{3}\pi I\alpha\cos\theta \quad \text{and} \quad -\tfrac{4}{3}\pi I\alpha\sin\theta.$$

But if we consider a neighbouring point just within the medium, while the magnetic forces due to the sphere will be the same as before those due to the medium will be

$$-\tfrac{8}{3}\pi I\alpha\cos\theta \quad \text{and} \quad -\tfrac{4}{3}\pi I\alpha\sin\theta.$$

The conditions which must be satisfied are that the total tangential magnetic force at a point between the distributions shall be the same as that at a neighbouring point within the medium, and that the density $-\alpha I\cos\theta$ of the surface distribution on the medium at any point shall be the product of K and the total radial magnetic force towards the centre at a neighbouring point just within the medium. The first condition is obviously satisfied, since each magnetic force is

$$\tfrac{4}{3}\pi I\sin\theta\,(1-\alpha).$$

The second condition gives

$$+\alpha I\cos\theta = K.\tfrac{8}{3}\pi I\cos\theta\,(1-\alpha)$$

or

$$3\alpha = 8\pi K\,(1-\alpha).$$

Hence $\alpha = 8\pi K/(3+8\pi K)$, and the factor $(1-\alpha)$ by which the magnetic force has been multiplied owing to the presence of the medium is $3/(3+8\pi K)$, which can be written as $3/(2\mu+1)$, and is *not* μ^{-1}. This result may be verified as follows.

When the sphere is surrounded by a vacuum, the value of H within it is given by

$$H = -\tfrac{4}{3}\pi I,$$

and $B = 4\pi I - \tfrac{4}{3}\pi I$, or $\tfrac{8}{3}\pi I$.

When the medium replaces the vacuum, the value of H within the sphere becomes

$$-\tfrac{4}{3}\pi I + \tfrac{4}{3}\pi I\alpha,$$

and the corresponding value of B is

$$\tfrac{4}{3}\pi I\,(2 + \alpha).$$

Hence the flux of B through the sphere is *increased* in the ratio $\tfrac{1}{2}(2 + \alpha)$ by the presence of the medium.

Since in the medium the magnetic force is μ^{-1} multiplied by the induction, the ratio of the new magnetic force to the old is $(2 + \alpha)/2\mu$, and this ratio is $(1 - \alpha)$.

The equation

$$2 + \alpha = 2\mu\,(1 - \alpha)$$

gives

$$1 - \alpha = 3/(2\mu + 1),$$

as before.

It will be noticed that this result is independent of the diameter of the sphere, and therefore that the statement whose accuracy we are challenging is not in general true even for a small magnet.

If we wish to consider the case of a uniformly magnetized sphere made not of an ideal substance whose magnetization is invariable but of some actual substance in which the forms of the graphs connecting the values of I and H are known, the comparison between the external magnetic force when the magnet is surrounded by a vacuum and the force when the vacuum is replaced by a magnetizable medium may be similarly effected.

It may be assumed that the sphere was magnetized by the production and subsequent removal of a strong uniform external field. Then, since the value of H within the magnet when surrounded by a vacuum is $-\tfrac{4}{3}\pi I$, the value of I, the "residual" magnetization, can be calculated by combining the equation

$$H = -\tfrac{4}{3}\pi I$$

with that part of the magnetization-field graph which relates to numerically increasing negative values of H, and we have already seen how the magnetic force at any external point in a vacuum can be calculated when I is known.

If the magnetizable medium is now allowed to take the place of the vacuum, the numerical value of the negative magnetic force within the magnet is decreased owing to the surface distribution over the medium, and I is consequently increased to I', whose value can be obtained from a suitably drawn magnetization-field graph relating to numerically decreasing negative values of H combined with the equation

$$H = -\tfrac{4}{3}\pi I\,(1 - \alpha),$$

where $1 - \alpha$ has the value already determined. We have already seen how the magnetic force at any point in the medium can be calculated in terms of the magnetization of the sphere, which in this case is I'.

When the magnet under consideration is not both spherical and uniformly

magnetized the changes of external magnetic force due to immersion in a magnetizable medium remain explicable in general terms by the application of exactly the same principles, although the difficulties of calculation become formidable. The direction as well as the magnitude of the magnetic force at a given point will in general be affected.

The case in which the magnet under consideration is a simple magnetic shell is of some interest, as in the course of an ancient controversy about the dimensions of units it was asserted without contradiction that the moment of the magnetic shell equivalent to a given current depended upon the medium surrounding the shell and was proportional to the permeability of this medium. If this statement were correct it would follow that the magnetic force at a given external point due ϕ to a simple magnetic shell of strength ϕ surrounded by a vacuum would be the same as that at a corresponding point due to a simple magnetic shell of strength $\mu\phi$ surrounded by a medium of permeability μ.

H_1 Now if H_1 is the magnetic force at a given external point due to the shell of strength ϕ surrounded by a vacuum, the magnetic force at a corresponding point due to a shell of strength $\mu\phi$ of the same form surrounded by the medium is, as H_2 we have seen, equal to the resultant of μH_1 and H_2, the magnetic force due to the surface distributions of magnetism over the boundaries of the medium, which are, of course, the positive and negative surfaces of the shell. If this resultant was at every point equal to H_1 in magnitude and direction the resulting equation

$$\mu H_1 + H_2 = H_1, \quad \text{or} \quad H_2 = H_1(1 - \mu)$$

would be equivalent to the assertion that the field of magnetic force due to the two surface distributions in contact with the positive and negative surfaces of the shell was the same as that due to a simple magnetic shell of the same form surrounded by a vacuum and of strength $-(\mu - 1)\phi$.

The actual surface distributions, however, cannot be equivalent to such a shell, nor indeed to any simple magnetic shell, for since they coincide in position with the two surfaces of the simple shell their distance apart is everywhere evanescent and their densities at all points would therefore have to be everywhere infinitely large in order to make such an equivalence possible. But it is clear that the actual surface densities of these distributions must be finite everywhere except at the edge of the shell, since they are given by the normal components of the magnetization of the medium near the shell, and the magnetic force in this region of the medium is finite.

It follows that the field of magnetic force around a simple magnetic shell surrounded by a magnetizable medium is *not* similar to the field of magnetic force of any simple magnetic shell surrounded by a vacuum.

DISCUSSION

Prof. W. WILSON. I have not had an opportunity to study Prof. Wilberforce's paper thoroughly; but I have definite views about the relationships between the magnetic quantities mentioned in it. It is well to think of them in terms of what I

call the magnetic displacement, D, a quantity analogous to Clerk Maxwell's electric displacement. We may regard it as a sum of two parts (I am thinking, for brevity, of an isotropic medium), one D_0 associated with empty space and the other I a contribution of the medium. Thus

$$D = D_0 + I.$$

It is easy to show that this is equivalent to

$$\mu H/4\pi = \mu_0 H/4\pi + I,$$

where μ is the permeability of the medium and μ_0 that of empty space. We may write this in the form

$$B = B_0 + 4\pi I \quad \text{or} \quad \mu = \mu_0 + 4\pi K.$$

It is a fundamental law of magnetism that div $B = 0$ always. I think it must be agreed that it follows from this law that when the (isotropic) medium surrounding a magnet is replaced by another such medium the value of B at a given point remains unchanged, provided of course that the magnetization of the magnet is maintained unchanged. Hence

$$\mu_0 H_0 = \mu H,$$

or if μ_0, the permeability of empty space, is chosen to be unity,

$$H_0 = \mu H.$$

If Prof. Wilberforce is not keeping the magnetization of his magnet constant, while changing the external medium, I fail to understand what is the problem he is dealing with.

Mr T. Smith. I understand Prof. Wilberforce's point is that in dealing with magnetic problems mistakes are made in the boundary conditions, not in the form of the functions involved. Could Prof. Wilberforce illustrate his paper by formulating the correct and the incorrect boundary conditions either generally or in a suitable soluble problem?

Author's reply. Prof. Wilson is mistaken in supposing that the B_0 in his equation $B = B_0 + 4\pi I$ is identical with the value that B would have at the point considered if the medium were replaced by empty space. If he considers the well-known case of a sphere of permeability μ in a uniform magnetic field he will find that this identity does not exist. It therefore does *not* follow that when the isotropic medium surrounding a magnet is replaced by another such medium the value of B at a given point remains unchanged, provided that the magnetization of the magnet is maintained unchanged, if by "magnetization" Prof. Wilson still means the quantity I.

If Mr T. Smith will refer to my paper he will find the correct boundary conditions formulated for the soluble problem of a uniformly magnetized sphere. The mistakes which have been made have not been due to incorrect formulation of such conditions but to the erroneous belief that a magnet of constant magnetization must in all circumstances have an invariable flux of magnetic induction through it.

THE MEASUREMENT OF SURFACE TENSION

By T. CARLTON SUTTON, Research Department,

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ABSTRACT. A convenient method is described for measuring simultaneously the surface tension and the density of a sample of liquid. A few milligrams of liquid will suffice. The method has advantages, therefore, for the measurement of the parachors, $\gamma^{\frac{1}{4}}/\rho$, of rare liquids. Volatile liquids may be used.

IN a paper read before the Physical Society* Dr Ferguson and Mr Kennedy discuss some methods of measuring the surface tension of liquids which are not available in large quantities. A description of an alternative method which I designed some two years ago may be of interest in this connexion; this method has been used for the measurement of parachors, and can readily be extended to the measurement of interfacial tensions. For the purpose in hand, it is important that (1) the volume of liquid should be small, and (2) the method should be independent of the density or (preferably) should give values of both the density and the surface tension of the sample.

Two tubes, differing in size of bore, are fused together. The liquid is then introduced so as to lie across the join and extend into the uniform portions of the tube. The tendency is for the liquid to pass into the tube of finer bore. If, however, the system is held vertically with the finer bore uppermost, this tendency is balanced by the weight of the column of liquid. A steady state is attained when†

$$\frac{\gamma}{2\pi r} - \frac{\gamma}{2\pi r'} = \rho g h,$$

r, r', ρ, h where γ is the surface tension, r, r' the radii, ρ the density and h the height of the column. If the dimensions of the tube are known this is sufficient to determine the surface tension in terms of the density. In practice, however, it is more convenient to connect the end of the tube to a gas-reservoir fitted to a manometer, and to proceed as follows.

Adjust the pressure in the reservoir so as to bring the meniscus to a chosen marked position L in the finer bore. A state of stable equilibrium is attained when

$$\left(\frac{\gamma}{2\pi r} - \frac{\gamma}{2\pi r'}\right) - \rho g l = p_1 \qquad \qquad \ldots\ldots(1),$$

l, p_1 where l is the vertical distance between the ends of the column of liquid and p_1 is the pressure recorded on the manometer.

The tube is then inverted so that the finer bore is now in the lower end. In this

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* *Proc. Phys. Soc.* **44**, 511 (1932).

α † If the liquid makes a contact angle α with the tube, γ should be replaced by $\gamma \cos \alpha$ throughout the equations.

position the capillary forces and the weight of the column both tend to draw the liquid downward. Equilibrium is attained when

$$\left(\frac{\gamma}{2\pi r} - \frac{\gamma}{2\pi r'}\right) + \rho g l = p_2 \qquad \ldots\ldots(2),$$

where p_2 is the pressure recorded on the manometer when the tube has been inverted in this way. $\qquad p_2$

This equilibrium, however, is unstable and the meniscus is brought to the chosen position by adjusting the pressure in the reservoir successively above and below p_2. Provided the finer bore is such that the viscous resistance of the liquid makes the movements within the tube appropriately slow, this measurement can be made with considerable precision.

To standardize the tube, a value is required for $(1/2\pi r - 1/2\pi r')$. This may be obtained by measuring the stable equilibrium given by relation (1) with a standard liquid in the tube. In most instances water or benzene may be used. By this means

$$\left(\frac{1}{2\pi r} - \frac{1}{2\pi r'}\right) = \frac{p' + \rho_s g l'}{\gamma_{\text{(standard)}}} = \frac{1}{k}, \text{ say,} \qquad k$$

where ρ_s is the density of the standard liquid, and p', l' are the corresponding $\qquad \rho_s, p', l'$ values obtained for p_1 and l.

The relations (1) and (2) may now be written in the convenient form:

$$\gamma = \tfrac{1}{2}k\,(p_1 + p_2) \qquad \ldots\ldots(3),$$
$$\rho = (p_2 - p_1)/2gl \qquad \ldots\ldots(4).$$

To compare the surface tensions of two liquids (3) may be written

$$\frac{\gamma}{\gamma'} = \frac{p_1 + p_2}{p_1' + p_2'} \qquad \ldots\ldots(5),$$

where γ', p_1' and p_2' refer to the second liquid. $\qquad \gamma', p_1', p_2'$

In this relation the dimensions of the capillary tubes have been eliminated, so that the measurements depend entirely on readings of the manometer attached to the gas-reservoir. The accuracy of the method depends therefore on (i) ensuring that the volume of liquid is constant and that the liquid is brought to the standard mark L, and (ii) employing a sensitive and reliable manometer.

Form A   Form B
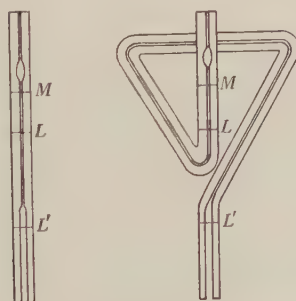
The apparatus may take various forms. If the liquid is scarce, the simple form A may be required. If the liquid is limpid as well as scarce, the necessary

resistance to motion is obtained by choosing tubes of fine bore. If more liquid is available, it may be found more convenient to obtain this resistance by bending a tube of somewhat coarser bore into the form *B*.

In either case, it is desirable that the tube should be provided with a means of obtaining a sample of standard volume. This is effected by making the finer tube somewhat longer than would otherwise be necessary, and blowing a small bulb about 1 cm. from the end (see diagram). If the liquid is now drawn into the tube to the fixed mark *M*, a fixed volume is obtained, which may subsequently be made to fill the equal volume bounded by the marks *L* and *L'*. Long tubes have the further advantage that evaporation is reduced to a minimum. The measured value of the surface tension under these conditions is that of the liquid in contact with an atmosphere saturated with its own vapour.

The table shows the consistency with which measurements on a particular sample of liquid can be repeated. Greater differences, however, occur between various samples of the same liquid.

Substance	Surface tension (dyne/cm.)	
	Author's value	From *Int. Crit. Tab.*
Benzene (purified) at 20° C.	28·9	
	29·05	
	28·75	
	Mean 28·9*	28·9
Toluene (commercial) at 18° C.	28·9	
	29·0	
	28·9	
	Mean 28·9	
Toluene (pure) at 20° C.	—	28·4
Water (laboratory supply) at 20° C.	72·8	
	73·6	
	73·5	
	72·6	
	Mean 73·1	
Water (pure) at 20° C.	—	72·8

* This value has been used provisionally to standardize the apparatus.

For many purposes, including the measurement of parachors, a measurement of density is needed on the same sample as is used for the measurement of surface tension. The present method has the advantage in this respect, that the density of the sample is given by relation (4) in terms of readings on the manometer and of a measurement of length which can be made readily by means of a travelling microscope.

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AN INVESTIGATION INTO THE FLOW
OF AIR IN PIPES

By B. LLOYD-EVANS, M.Sc. (Eng.), M.I.Mech.E. and
S. S. WATTS, B.Sc. (Eng.), University College, London

ABSTRACT. The authors examine the researches of Ombeck on the flow of air through cylindrical pipes, and obtain an expression which represents in a convenient form the phenomena that occur in a smooth-bore pipe. In particular, they separate the effects of acceleration of the gas from those of friction, and express the latter in terms of the equation suggested by Lees to fit Stanton's curve. Their results appear to justify the researches of Lees and Stanton, rather than the analysis made by Ombeck of his test figures.

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§1. INTRODUCTION

IN order to investigate the pressure-changes in steam turbine nozzles and blading, it is necessary to consider the effects of both friction and acceleration. As these two effects can be separated most easily in the case of a parallel pipe, it was considered advisable to refer to the work of Stanton[*] and Ombeck[†].

While the curves of Stanton for $R/\rho S^2$ (where R represents the frictional resistance per unit area of pipe surface, ρ the density and S the velocity of the gas) against what is commonly termed the "Reynolds's number," $\rho SD/\mu$ (where D is the diameter and μ the viscosity), do not show any test points for a compressible fluid in which the acceleration term is of marked importance, the investigations of Ombeck include an analysis of the effect of the acceleration of the gas, especially in the figures quoted from his tests in group 1, series 2, table 5. A summary of this particular set of tests is given on p. 99 of this paper. In these tests the acceleration term is relatively large, and fortunately the measured test values corresponding to tests nos. 1, 7 and 16 of this series are given in greater detail in diagrams 16, 17 and 18 on pages 25 and 26 of his work. As it is difficult to discover any relation between these diagrams and the values of "measured pressure-drop per metre of pipe length" quoted on page 44, column 7, table 5, the authors have been able to analyse only tests nos. 1, 7 and 16 in accordance with their theory.

On page 23, *loc. cit.*, Ombeck appears to consider the action of acceleration without allowing for the effect of friction, whereas these two effects are present together in an actual pipe carrying an expansible fluid, and the following theory has been developed to cover both actions.

R

ρ, S

D

μ

  * *Phil. Trans.* A, **214**, 199 (1925).
  † *ForschArb. Ingenieurw.* Nos. 158 and 159 (1914).

§2. THEORY

dl   Let the initial conditions over a short length of pipe *dl* be as follows:

P P is the pressure (dynes per cm.^{2} of cross-section);

V V the specific volume (cm.^{3}/gm.);

S S the velocity (cm./sec.);

U U the internal energy per gram of gas (heat units); and

T T the absolute temperature (° C.);

for the motion of the centre of gravity of the gas per gram flowing

$$PV + \tfrac{1}{2}S^2 + JU = (P + dP)(V + dV) + \tfrac{1}{2}(S + dS)^2$$
$$+ J(U + dU) + JdQ \quad \ldots\ldots(1)^*,$$

dQ   where *dQ* is the heat lost over the length *dl* of pipe.

Therefore $0 = PdV + VdP + SdS + JdU + JdQ$ $\ldots\ldots(2).$

dF   Now the pressure-drop *dF* due to friction is given by

$$dF = R \times \text{wetted surface} \div \text{cross-section of pipe},$$

R   where R has the same meaning as in Stanton's curve; and Lees[†] has expressed R (in dynes/cm.^{2} of wetted surface) thus

$$R = \rho S^2 \{0.0765\,(\mu/S\rho D)^{0.35} + 0.0009\}.$$

Therefore $dF = R \times \pi Ddl \div \tfrac{1}{4}\pi D^2$

$$= (4\rho S^2 dl/D)\{0.0765\,(\mu/S\rho D)^{0.35} + 0.0009\} \quad \ldots\ldots(3).$$

Now $J(dH - dQ) = PdV + JdU$ $\ldots\ldots(4),$

dH, dU   where *dH* is the heat added by friction per gram and *dU* is the increase of internal energy of the gas; and the work lost in friction per gram flowing is *dF* ρ. Therefore by inserting (3) and (4) in equation (2) we have

$$-VdP = SdS + (4S^2 dl/D)\{0.0765\,(\mu/S\rho D)^{0.35} + 0.0009\} \quad \ldots\ldots(5).$$

M, A   If M is the mass of gas flowing per second, in grams, and A the cross-sectional area of the pipe in cm.^{2}, then

$$S^2 = M^2 V^2 / A^2,$$

for continuity.

Also we can write

$$PV = rT \text{ per gram of gas,}$$

and if we assume for the moment that the law of the expansion of the gas down the pipe is

$$PV^n = C_2[‡],$$

C₂   where C_2 is a constant, then

$$-VdP = d(M^2 r^2 T^2 / 2A^2 P^2) + (4dl/D)(MrT/A)^2 \lambda$$

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[*] For the development of this equation see Zeuner, *Technical Thermodynamics*, **1**, 273; A. Stodola, *Steam and Gas Turbines*, **1**, 38 (English edition); A. B. Eason, *Flow and Measurement of Air and Gases*, Chap. 11 (1st edition).

[†] C. H. Lees, *Proc. R. S.* A, **91**, 46 (1914).

[‡] This is discussed in detail in the Appendix.

where $\qquad\qquad\qquad \lambda = 0.0765\,(\mu/S\rho D)^{0.35} + 0.0009$ $\qquad\qquad\qquad\qquad\qquad\quad \lambda$

and $\qquad\qquad\qquad\quad T = C_1 P^{(1-1/n)},$ $\qquad\qquad\qquad\qquad\qquad\qquad C_1$

or $\qquad - VdP = (M^2 r^2/2A^2)\,d\,(T^2/P^2) + \lambda dl\,(64 M^2 r^2 T^2/\pi^2 D^5 P^2)$

$$= (8 M^2 r^2/\pi^2 D^4)\,d\,\{C_1^2 P^{2(1-1/n)}/P^2\}$$
$$+ \{64 M^2 r^2 C_1^2 P^{2(1-1/n)}/\pi^2 D^5 P^2\}\,\lambda dl.$$

So that $\qquad\qquad - VdP = K_1 dP^{-2/n} + K_2 dlP^{-2/n}\,\lambda \qquad\qquad ......(6),$

where $\qquad\qquad\qquad K_1 = 8 M^2 r^2 C_1^2/\pi^2 D^4$

$$K_2 = 64 M^2 r^2 C_1^2/\pi^2 D^5 = 8 K_1/D,$$

and λ can be written as $0.0765\,(\mu\pi D/4M)^{0.35} + 0.0009$, which will be considered as constant for the small changes in temperature existing in actual pipe lines.

Rearranging equation (6) and integrating along the length L of the pipe we have

$$8 K_1 \lambda dl/D = -C_2^{1/n}\,dP/P^{-1/n} - K_1\,dP^{-2/n}/P^{-2/n}$$

and $\qquad 8 K_1 L\lambda/D = -C_2^{1/n}\left(\dfrac{n}{n+1}\right)P^{(1+1/n)}\Big]_{P_1}^{P_2} - K_1 \log_e P^{-2/n}\Big]_{P_1}^{P_2}$

$$= C_2^{1/n}\left(\frac{n}{n+1}\right)(P_1^{(1+1/n)} - P_2^{(1+1/n)}) - (2 K_1/n)\log_e (P_1/P_2).$$

Therefore $\qquad \lambda = (D/4L)\,[\{\pi^2 D^4 n/16 M^2 r\,(n+1)\}\,\{P_1^2/T_1 - P_2^2/T_2\}$
$$- n^{-1}\log_e (P_1/P_2)]\ ......(7).$$

In the above equation the term $n^{-1}\log_e (P_1/P_2)$ corresponds to the acceleration effect, and λ plotted against log (Reynolds's number) should fall on Stanton's curve. Equation (7) will be true in the case where $n = 1$, and therefore when the temperature along the pipe is constant.

§3. APPLICATION OF THE THEORY TO OMBECK'S RESULTS

Applying equation (7) to Ombeck's test point no. 1, previously referred to on page 91 of this paper, the value of the index n in the expansion $PV^n = C$ is determined by plotting log P against log T, with the numerical values given by Ombeck on page 26 of his paper. The slope of the resulting straight line gives a mean value of 1.192 for n.

The initial and final conditions, denoted by the subscripts 1 and 2 respectively, were as follows:

$$P_1 = 1945.2 \text{ gm./cm.}^2 \text{ or } 19.08 \times 10^5 \text{ dyne/cm.}^2;$$
$$P_2 = 1123.6 \text{ gm./cm.}^2 \text{ or } 11.01 \times 10^5 \text{ dyne/cm.}^2;$$
$$T_1 = 280° \text{ K.}; \mu = 1.775 \times 10^{-4} \text{ c.g.s.u.}^*;$$
$$T_2 = 256.7° \text{ K.}; \mu = 1.625 \times 10^{-4} \text{ c.g.s.u.}^*.$$

The pipe-diameter is given as 2.004 cm., and the length over which P_1 and P_2 are measured is 134.5 cm.

* Values of μ obtained from *The Mechanical Properties of Fluids*, p. 112 (Blackie).

The mass of air flowing is 131·2 gm./sec. and r for air may be taken as 2·88 × 10^6 c.g.s.u. Therefore

$$\lambda = 0·001648,$$

and Reynolds's number = 83·4/μ.

In the above example the friction and acceleration effects are approximately equal, their relative importance being given numerically by the terms 0·4446 for friction and 0·4614 for acceleration, so that friction/acceleration = 0·963.

The two values of log (Reynolds's number) corresponding to inlet and outlet temperature conditions are 5·672 and 5·710, and the mean value is plotted on figure 1 and marked "I," together with points nos. 7 and 16 determined in exactly the same manner. Owing to slight differences in the values of μ taken by Ombeck, the Reynolds's numbers quoted by him do not agree exactly with those calculated by the authors.

A further analysis was made of Ombeck's figures as quoted by him in table 5, page 45, of his paper and collected in table 1 of this paper, equation (7) being used in a slightly different form, while λ was calculated as follows on the assumption of a constant temperature over the metre length of pipe. Using the same notation as before, with these additions, we have

$$P = \tfrac{1}{2}(P_1 + P_2);$$

δP = measured pressure-drop per metre;

$$\lambda = (D/4L)\,[\pi^2 D^4 P \delta P/16\,M^2 r T - \log_e (P_1 P_2)] \qquad ......(8).$$

The results of these calculations are shown in table 1 and plotted on figure 1, giving the curve marked "II," which departs radically from Stanton's curve (I).
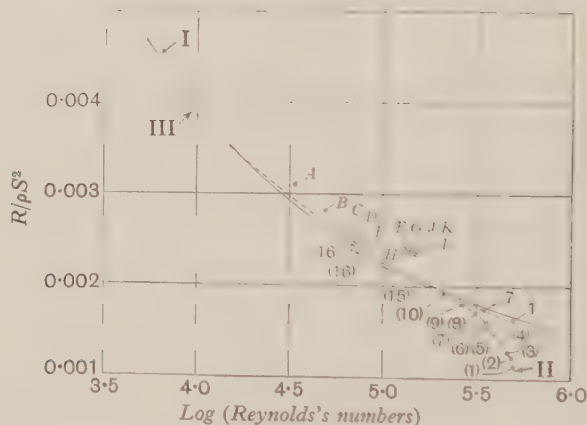

Figure 1.

This indicates the great importance of taking into account the actual value of n in the law of the expansion existing in the pipe. It also appears that Ombeck's method of separating the friction and acceleration effects is not accurate.

It was also noted on page 27 of Ombeck's paper that he has plotted log α

against log (Reynolds's number), where $\alpha = 2g\,Dh/Ls^2 = 2g\,(D\,\delta P/L\rho s^2)$, and δP is in gravitational units. Now $R/\rho S^2$ as plotted by Stanton may be written as

$$\delta P \times \pi D^2/4\pi D\,L\rho\,S^2 \quad\text{or}\quad \tfrac{1}{4}\,(D\,\delta P/L\rho\,S^2).$$

When δP is in absolute units, $\alpha = 8R/\rho S^2$.

This allows the graph on page 27 of Ombeck's paper to be transferred to figure 1, where it is shown as curve III, agreeing fairly closely with Lees's form of Stanton's curve I over a range of Reynolds's numbers from 15,000 to 250,000.

The accuracy, however, of the results obtained by plotting the logarithms in this manner and drawing a straight line through the test points is open to question, as has been pointed out by Kerr*.

§4. EXPERIMENTS BY THE AUTHORS

Owing to the difficulty of obtaining sufficient particulars of tests where the acceleration term becomes of importance, the authors decided to carry out a number of experiments with this in view. Unfortunately the size of the compressor available limited the diameter of the pipe under test.
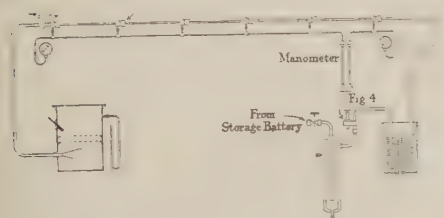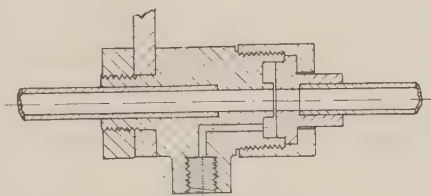

Figure 2.

Figure 3. The gap between pipe ends for pressure-tapping is about 0·007 in.

The arrangement of the pipe line and associated apparatus is shown in figure 2. The pipe tested was nominally $\tfrac{3}{8}$ in. in outside diameter, of solid drawn copper, with 16 i.s.w.g. walls. The actual bore was obtained by plugging the ends of each length, filling with water, and weighing. The five lengths to be tested were each 6 ft. long, as also was the inlet length, which was of the same diameter; all the lengths were drawn from the same batch to ensure uniformity, and great care was taken to see that each length was initially straight. At the ends, and between each two lengths, a pressure box (figure 3) was arranged and was coupled by means of a needle valve to a common bus-pipe, which was connected either to a pressure gauge or to one limb of a mercury manometer, the other limb of which was connected to the first pressure box. The pressure-drop along any multiple of 6 ft. up to a length of 30 ft. could thus be determined. The inlet pressure was read on a Bourdon gauge, the calibration of which was checked before and after each series of readings.

This pressure was maintained constant by means of a single-lever reducing

* "On Turbine Wheel Friction", *J. Royal Technical College, Glasgow* (1923).

valve (figure 4), and the drop of pressure along the pipe was controlled by a sensitive screw-down valve, supplemented by a special spring-loaded control valve (figure 5) arranged in parallel with it for tests requiring small pressure-differences. The air-supply was drawn from a reservoir consisting of a battery of three torpedo receivers which could be charged from a two-stage compressor to a pressure of 200 lb./in². In all tests except those in which a very large quantity of air was flowing the receivers were allowed to stand, after charging, until the temperature was steady. For the higher rates of flow, however, it was necessary simultaneously to run the compressor, a water-cooled coil and moisture-trap being fitted in series with the pipe line; this coil enabling the temperature at inlet to the pipe to be equalized with that of the surrounding atmosphere. The effects due to radiation could thus be eliminated.
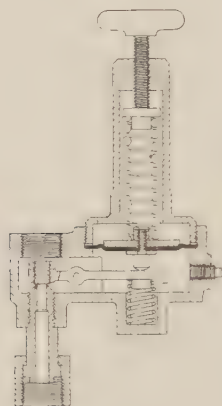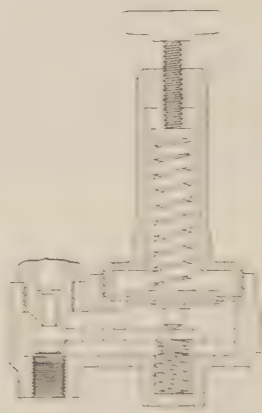

Figure 4.   Figure 5.

As it was considered necessary to take instantaneous readings wherever practicable, the method finally adopted for measuring the air flow utilized an orifice meter consisting of a number of sharp-edged orifices ⅜ in. in diameter, symmetrically disposed in the end of a drum and discharging into the atmosphere. The head across the orifices was measured by a water manometer, and the number of orifices in use was adjusted to keep this head below 7 in. of water for all the tests.

As an alternative, in the case of very small flows, a drum meter of the wet type, previously calibrated by a water-displacement method, was used. The coefficient of discharge of the orifices was obtained by comparison with the drum meter. Thus it was anticipated that even if the measurements were not made with great accuracy, the results should agree amongst themselves and therefore allow equation (7) to be checked.

The procedure adopted for each test was to choose an inlet pressure, and determine the pressure-drop for a number of different quantities of air flowing. Originally measurements were made over each 6-ft. length of pipe under test; but it was found that the results for the varying lengths agreed satisfactorily, so finally the measurements were made over the complete pipe-length.

§5. AUTHORS' RESULTS

Curve VI of figure 6 shows the type of curve obtained by plotting the drop of pressure against the quantity of air passing. From these graphs values were taken from which the ordinates for Stanton's curve were calculated. The points so chosen are indicated on figure 1 by the letters A, B, C, ..., the tabular values of these results being shown in table 2. In the above tests, the temperature was found to be sensibly constant along the length of the pipe.
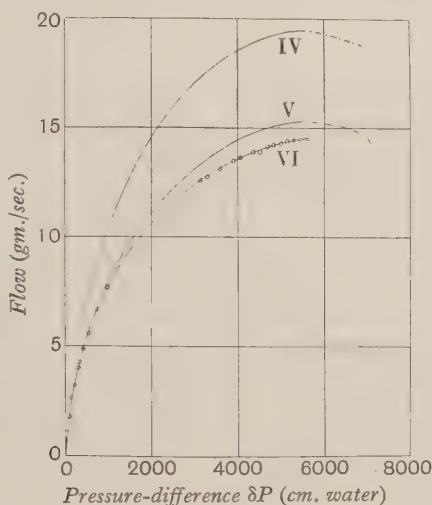

Figure 6.

The points appear to be on a curve of the type predicted by Stanton, although minor disturbances caused by the pressure boxes produced a slight increase in resistance. Curve V of figure 6 shows the mass of air plotted against the drop of pressure along the pipe, obtained by solving equation (7) for the authors' pipe line, with a fixed inlet pressure of 7220 cm. of water gauge (absolute) and a temperature of 18·8° C., Lees's values being taken for λ. It will be noted that this curve rises to a maximum and then falls again. Unfortunately it is not possible to make tests after the maximum has been reached, as the pressure at the outlet is then below the atmospheric pressure, and a vacuum pump sufficiently large to deal with this quantity of air appears impracticable. It is of interest, however, that this result might have been obtained by differentiation of equation (7), M and P_2 being assumed to vary while all the other factors remain constant. Writing

$$C_1 = T_1/P_1^{(1-1/n)} \qquad\qquad C_1$$

we have

$$\lambda = 0\cdot0765\,(\mu\pi D/4M)^{0\cdot35} + 0\cdot0009 = (D/4L)\,[\{A^2 n/M^2 r\,C_1\,(n+1)\}$$
$$\times\{P_1^{(1+1/n)} - P_2^{(1+1/n)}\} - n^{-1}\log_e(P_1/P_2)],$$

where $A = \pi D^2/4$ and is the cross-sectional area of the pipe. $\qquad A$

Or if K_1, K_2, K_3 are constants, $\qquad\qquad K_1, K_2, K_3$

$$K_1 M^{-0\cdot35} + K_2 = K_3 M^{-2} P_1^{(1+1/n)} - K_3 M^{-2} P_2^{(1+1/n)} + (D/4Ln)\log_e P_2;$$

7

and differentiating with respect to P_2, collecting terms containing dM/dP_2 and equating to zero for a maximum, we have

$$- 0 \cdot 35\, K_1 M^{-1 \cdot 35}\, dM/dP_2 = -\, 2K_3 P_1^{(1+1/n)}\, M^{-3}\, dM/dP_2$$

$$-\, K_3\{-\, 2M^{-3}P_2^{(1+1/n)}\, dM/dP_2 + M^{-2}P_2^{1/n} \times (n+1)/n\} + D/4 Ln P_2,$$

whence $\qquad\qquad -\, K_3 M^{-2} P_2^{1/n} \times (n+1)/n + D/4 Ln P_2 = 0.$

Therefore $\qquad\qquad D/4 Ln P_2 = (D/4L)\,(A^2/M^2)\, P_2^{1/n}/rC_1,$

or $\qquad\qquad\qquad M^2/A^2 = nP_2^2/rT_2,$

and since $\qquad\qquad P_2 = \rho_2 rT_2 \quad \text{and} \quad (M/A) = S_2\rho_2,$

$$S_2^2\rho_2^2 = n\rho_2^2 rT_2 \quad \text{and} \quad S_2 = \sqrt{(nrT_2)} \qquad \ldots\ldots(9).$$

The maximum value possible for S_2 is therefore $\sqrt{(\gamma rT_2)}$, corresponding to adiabatic

γ flow when n becomes γ, the ratio of the specific heats. Now this is the velocity of sound in the air at the outlet conditions, a result to be expected by comparison with nozzle flow.

For conditions other than adiabatic the maximum flow is determined by another form of equation, derived from equation (7). If the flow is isothermal this reduces to

$$M_{(\text{maximum})} = A \sqrt{(\rho_2 P_2)} \qquad \ldots\ldots(10).$$

Considering a fixed set of conditions for the inlet pressure and temperature in a pipe, and assuming isothermal flow, we obtain curves IV and V of figure 6 by solution of equation (7) for 18-ft. and 30-ft. lengths of pipe respectively. In both cases isothermal flow was assumed, as this approximates most nearly to the authors' tests. The corresponding curve for the tests is shown by curve VI, relating to a 30-ft. pipe. The difference between curves V and VI is due to the pressure-box connexions, as has already been explained. It is to be noted that both curves show definite maximum flows at which equation (10) is satisfied. It is open to discussion whether the actual form of the curve would be as shown, after the maximum point is reached, or whether the flow would remain approximately constant as in the case of a nozzle.

For reasons already given, the maximum value of Reynolds's number which the authors were able to obtain was 153,000, corresponding to a terminal velocity of 23,000 cm./sec.

The agreement between curves V and VI in figure 6 is sufficiently good to prove that either equation (7) or equation (8) may be used for predicting the flow in a pipe line for conditions approximating to the isothermal condition, provided that the roughness of the inner pipe surface justifies the use of Lees's equation. In cases where an "artificial" temperature-gradient obtains along the length of the pipe, allowance must be made for variations in the coefficient of viscosity.

One important case where this applies is in the heat-exchangers of plants used in the manufacture of liquid air and oxygen. So far as the authors are aware, there are no figures enabling the viscosity of air to be expressed as a function of the temperature under these low-temperature conditions, and they hope to be in a position to investigate this problem shortly.

Table 1

Test no.	Quantity flowing (gm./sec.)	Mean pressure (mm. water)	Mean temperature (° K.)	Measured pressure-drop per metre (mm. water)	Reynolds's number	log (Reynolds's number)	Calculated values of $R/\rho S^2$
			Values extracted from Ombeck's paper				
1	131·2		269·4	7200	449,862	5·6954	·00114
2	127·5		269·5	6475	481,496	5·6826	·00123
3	121·7		271·7	5438·5	456,760	5·6597	·001296
4	116·4	14,365	273·2	4737·5	434,479	5·6380	·001384
5	107·9		276·0	3812·5	399,323	5·6103	·001484
6	100·7		278·6	3161·5	369,634	5·5678	·001554
7	97·07		279·6	2912·5	355,446	5·5508	·001617
8	85·54		282·9	2125·0	310,382	5·4919	·001708
9	73·67	14,375	285·8	1525·0	264,930	5·4231	·001814
10	58·69		289·6	937·5	209,029	5·3202	·00192
15	29·77	14,385	293·2	249·2	104,973	5·0211	·002184
16	20·96		294·3	130·8	73,714	4·8676	·00236

Table 2

Test point	Quantity flowing (gm./sec.)	Inlet pressure (mm. water)	Temperature (° K.)	Measured pressure-drop* (mm. water)	Reynolds's number	log (Reynolds's number)	$R/\rho S^2$
A	3·173	72,000	291·8	2,000	33,500	4·525	·0031
B	4·67	,,	,,	4,000	49,300	4·6928	·00282
C	5·85	,,	,,	6,000	61,750	4·7907	·002654
D	6·892	,,	,,	8,000	72,800	4·8621	·002505
E	7·62	,,	,,	10,000	80,440	4·9055	·002523
F	12·25	,,	,,	30,000	129,300	5·1116	·00242
G	12·81	,,	,,	34,000	135,300	5·1313	·002403
H	13·3	,,	,,	38,000	140,400	5·1475	·002377
J	13·7	,,	,,	42,000	144,600	5·1602	·002361
K	14·02	,,	,,	46,000	148,000	5·1703	·00235
L	14·25	,,	,,	50,000	150,400	5·1772	·002344

* On a 30-ft. length of pipe.

APPENDIX

In the foregoing pages the assumption has been made that the relation between pressure and volume along a pipe line is given by

$$PV^n = \text{constant.}$$

This assumption will now be discussed in more detail.

In the case of a "perfect" gas for which $\partial U/\partial P = 0 = \partial U/\partial V$, we may write $dU = K_v dT$, where K_v is the specific heat at constant volume, so that equation (2) on page 92 can be written

$$d(PV) + \tfrac{1}{2}dS^2 + JK_v dT + f(T)\,dl = 0,$$

where $f(T)\, dl$ represents the exchange of heat per gram flowing between the gas and the pipe wall, over the length dl under consideration in the pipe line; and since $f(T)$ cannot be expressed simply in terms of T, it is impossible to make use of this equation except in the simple case of an insulated pipe where $f(T) = 0$.

In this case, we have

$$d(PV) + \tfrac{1}{2}dS^2 + \frac{JK_v}{r}d(PV) = 0,$$

or

$$\frac{JK_v}{r}d(PV) = -\frac{dS^2}{2} = -\frac{M^2}{2A^2}d(V^2),$$

so that

$$\frac{J}{r}K_P(P_1V_1 - PV) = \frac{M^2}{2A^2}(V^2 - V_1^2) \qquad \ldots\ldots(11),$$

where P_1 and V_1 relate to the known inlet conditions. This can be represented graphically by a hyperbola but not by an equation of the form PV^n constant.

Again, for an insulated pipe, the following equation can be derived connecting L, the pipe-length, and the specific volume at outlet in terms of M for a given set of inlet conditions:

$$8\lambda L/D = \{A^2P_1/M^2V_1 + (\gamma - 1)/2\gamma\}(1 + V_1^2/V^2) + (1 + 1/\gamma)\log_e(V_1/V)$$
$$\ldots\ldots(12).$$

On elimination of V from equations (11) and (12), a relation could be obtained giving M in terms of the outlet pressure P.

Unfortunately the above equations become too formidable when many numerical calculations are involved.

VIBRATIONS PRODUCED IN BODIES BY CONTACT WITH SOLID CARBON DIOXIDE

By MARY D. WALLER, B.Sc.

ABSTRACT. The paper describes the conditions under which very loud notes may be produced and maintained for a considerable time in metal objects capable of vibration, such as tuning forks, bars, discs, rings, and tubes, when brought into contact with a solid carbon dioxide block. Notes have also been sustained in quartz crystals. It is shown that the vibration frequencies normally excited may range from about 1000 to 15000 $\sim$. Lower frequencies have been excited in wires. Surface-tension ripples may be produced on mercury. The vibrations are only produced by solid carbon dioxide of high density. The physical properties of the vibrating body which are of importance in connexion with the phenomenon are considered. Evidence is brought forward in favour of the view that the source of energy for producing the vibrations is the heat which is given up by the metal to the solid carbon dioxide, and that the efficacy of this substance in producing vibrations is determined by the fact that it sublimes and in so doing produces considerable gas-pressures. Some suggestions regarding possible applications of the phenomenon are made.

§ 1. VIBRATIONS OF AUDIBLE FREQUENCY PRODUCED IN VARIOUS BODIES

IF a solid block of carbon dioxide be held against a metal, a rattling or singing sound, due to vibrations of the latter, will often be heard. This fact is familiar to some of those who handle carbon dioxide commercially.

In the course of an experimental investigation of the phenomenon it was at first found that no noise could be produced in glass bars and vessels, although they had good vibrating properties, and it was concluded that this was on account of the low thermal conductivity of glass. The next objects tried were tuning forks of the ordinary frequencies. These gave out a chattering noise. When, however, forks of higher frequency were tried, loud pure notes were excited. A demonstration of the phenomenon was given at the York Meeting of the British Association, 1932.

It may be stated, in anticipation of results to be described later, that the physical properties desirable in the body to be set into vibration in this manner are a suitable natural period of vibration, high thermal conductivity and elasticity, a small damping factor, and hardness; and, for maintaining vibrations in small bodies of a given size, a high specific heat and specific gravity. The observations that have been made on bodies of various shapes, masses and materials are described below.

(a) Tuning forks. Range of frequencies: 100 to 10000 $\sim$.

If a block of solid carbon dioxide of high specific gravity (see § 2 below) be brought into contact with the tip of one of the prongs of a tuning fork of high frequency, e.g. 3000 $\sim$, the fork will be set into violent vibration, and, if it is

massive, will give out a very loud piercing note. The fork should be held with a corner of one of the prongs lightly touching the block; sometimes a better result is obtained when a small portion of an edge a short way down the prong touches the block. Contact, but contact of a small area only, is essential. If a large area touches the block there may be much noise, which will diminish and cease when the surface of the block has become smooth and flat. The rate at which the solid carbon dioxide sublimes is visibly accelerated greatly during vibration of the fork.

If the fork be held skilfully, and gradually moved over the surface of the block so as to adjust the contact suitably, a loud note can be maintained for a minute or more, but only if there is no chattering.

The results obtained with tuning forks of different pitches are given in table 1, and it is evident that vibrations of higher frequency are more readily excited and maintained than those of lower frequency. Thus, with forks of low pitch it is the first overtone, and not the fundamental, that is excited. It should be noted that the ratio of frequency of the first overtone to that of the fundamental of a fork may vary from 5·8 to 6·6 (Helmholtz)*.

Table 1. Tuning forks

Natural frequency	Vibrations produced		Mass (gm.)	Duration of audibility (sec.)	Remarks
	Funda-mental	First overtone			
100	Chattering	610	230	70	$n_2/n_1 = 6\cdot08$
256	,,	1600	158	40	$n_2/n_1 = 6\cdot21$
512	,,	3200	60	50	$n_2/n_1 = 6\cdot21$
1024	1024	Audible	219	24	Difficult to maintain
1024	1024	,,	32	20	,,
2000	2000	,,	17	14	Loud, some chattering, maintained
2040	2040	,,	28	10	Clear, some chattering, difficult to maintain
3000	3000	—	275	28	Very loud, maintained
4000	4000	—	242	16	,,
5000	5000	—	196	11·5	,,
10000	10000	—	159	3	Very loud, difficult to excite and maintain

The masses of the forks and duration of audibility are given in the table because these quantities affect the ease with which the vibrations can be maintained and will be considered in the theory of the phenomenon.

The *duration of audibility* is defined for purposes of the present investigation as the number of seconds during which the vibrations from a body remain audible to the same observer when the body is situated near one ear, after it has been set vibrating vigorously. The figure indicates roughly that which a knowledge of the modulus of decay or time constant of a damped vibration would convey accurately

* J. Tyndall, *On Sound*, 138.

regarding the vibration properties of the body. In view of the nature of the present investigation, it has not been considered necessary to make allowance for the change of sensitivity of the ear for different frequencies.

Thus different bodies, made of the same material, will vary in their resonant properties because of their shape and mass; while bodies which are similar in the latter properties but are made of various materials will have different resonant qualities depending upon the internal damping forces of solid viscosity. The figures given are each the mean of several values which may vary among themselves by from 10 per cent to 20 per cent.

(b) *Brass bars.* Range of frequencies: 1950 to 15000 ∼.

The results obtained with a series of twelve rectangular bars, of square cross-section (1·27 × 1·27 cm.²) excited in a similar fashion to the tuning forks, are given in table 2. The note generally given out by such relatively short stout bars corresponds to a transverse vibration with two nodes. The bars were suspended by threads from the nodes (about $\frac{1}{4}$ of the length from either end); the positions of these could be made apparent by sprinkling sand on the upper surface, and then setting the bars in vibration.

Table 2. Brass bars

| Length (cm.) | Frequency | | Duration of audibility (sec.) | Remarks |
	Measured with sonometer	Calculated		
15·1	1950	1950	20	
12·7	2620	2780	17	
12	3200	3100	13	Very loud, maintained
11·5	3300	3390	11	
10·9	3500	3780	9	
10·2	4200	4300	10·8	Sometimes excited, very
9·5	4700	4970	7	loud, maintained
9·1	—	5400	4·9	
8·8	—	5800	4	
8·5	—	6200	4·4	
8·1	—	6800	3·8	Difficult to excite
7·7	—	7600	3·8	
6·5	—	10000	2	
5·25	—	15000	0·4	

The frequencies as determined practically with a sonometer and forks agree reasonably with the values calculated from the formula given by Rayleigh* for a free-free bar of rectangular cross-section. Thus for brass, the frequency

$$n = \tfrac{2}{3} \times 538400 \times t/l^2,$$

where t is the thickness, and l the length of the bar.

With some blocks of carbon dioxide frequencies up to 4300, and with others frequencies up to 6200, were easily excited and maintained, by touching the bars either at an end or at the centre. The difficulty of exciting higher frequencies is

* Rayleigh, *Theory of Sound*, 1, 279.

probably partly due to the smallness of the time constant rather than to the high value of the frequency. The longest bar weighed 200 gm. The figures given and statements made in the tables are of a somewhat general nature on account of the varying behaviour of different samples of solid carbon dioxide (see § 2).

Table 3 shows how the time constant diminishes with increasing cross-section of bars of equal length, and how this property partly controls the ease with which vibrations may be excited with solid carbon dioxide.

Table 3. Brass bars of square cross-section, and of length 11·5 cm.

Thickness (cm.)	Frequency	Duration of audibility (sec.)	Remarks
1·27	3330	10	Very loud, maintained
2	5230	5	Very loud, difficult to excite, maintained
2·5	7100	4	Very difficult to excite or maintain

(c) *Steel bars*. Range of frequencies: 4440 to supersonic.

Twenty-one steel bars of circular cross-section and of radius 1 cm. were available. The first fifteen bars, ranging from 15·1 cm. down to 7·7 cm. in length, were suspended and excited in the same manner as the brass bars (b). The frequencies as calculated ranged from 4450 to 18000 ~, and the duration of audibility diminished from 5·5 down to 1·8 sec. The bars were harder to excite than the brass bars on account probably of the smaller time constants, but piercing and maintained notes were sometimes obtained, especially when the bars were first of all struck with a hammer so that they were already vibrating before application of the carbon dioxide. The highest bar maintained was the tenth of the series having a (calculated) frequency of 11200 ~.

(d) *Longer bars*. Transverse overtones and longitudinal vibrations.

It would be of interest to carry out more observations on longer bars, which often vibrate in three or more audible modes simultaneously. The results so far obtained will not be described in detail, but two remarks will be made. (1) As in the case of tuning forks, a low-frequency bar is inclined to chatter, but an overtone (transverse vibration) can usually be produced. (2) It is possible to excite longitudinal vibrations. For example, in the case of three brass bars of lengths 100, 38 and 23 cm. respectively, the corresponding longitudinal vibrations of 1760, 4900 and 8000 ~ were produced, but were not maintained for any considerable length of time. Similarly an aluminium bar of length 91 cm. vibrated longitudinally with a frequency of 2660 ~. It will be noted that the bars have been so chosen that the frequencies are comparable with those of the transverse vibrations produced in short bars; the longitudinal vibrations of the latter were of course supersonic.

(e) *Metal plates*. Chladni sand figures.

Thin plates, of either rectangular or circular cross-section, e.g. the usual Chladni plates 4, 8 or 12 in. in diameter and 2 mm. in thickness, which give numerous

sand patterns when bowed, could generally only be excited to give out a confused noise with the block of carbon dioxide, though overtones could sometimes be picked out. On the other hand, loud notes were obtained with smaller and thicker discs which are not easily excited by bowing. Chladni sand figures may be produced, and a photograph of one of these is shown in the plate.

The data relating to six brass blanks are given in table 4, which also includes observations made on copper and zinc discs. It is to be noted that although copper conducts heat three times as well as brass and has a modulus of elasticity and density nearly equal to that of brass, its vibrating properties are inferior on account of internal friction. On the whole its capacity for vibrating in contact with carbon dioxide is about equal to that of brass. The frequencies were determined by means of a sonometer except in the case of no. 7, the frequency of which was compared with those of the series of brass and steel rods; see (*b*) and (*c*) above. Its frequency was also calculated from the approximate relation that the frequency of the discs varies directly as the thickness and inversely as the square of the radius. The discs were held centrally between finger and thumb. Irregular shaped thin discs, such as brass cymbals, may be excited to give out noise, while, e.g., a thick silver dish may give out a noise that has been likened to that of a pneumatic street drill!

Table 4. Metal discs

Number of disc	Material	Radius (cm.)	Thickness (mm.)	Frequency	Duration of audibility (sec.)	Remarks
1	Brass	10	5	1600	21	Very loud, maintained
2	,,	8·8	5	2200	14	
3	,,	7·6	5	2960	11	
4	,,	6·9	5	3260	8	
5	,,	5	5	7750	2	Difficult to excite
6	,,	2·5	5	Supersonic	—	—
7	,,	5	2	3100	5	Loud, maintained
8	Copper	7·6	5	2970	2	Very similar to no. 3
9	,,	7·6	3	3820	2	Clear, maintained
10	Zinc	7·6	3	4000	0·5	,,

(*f*) *Bars of various materials.*

Several materials were tried in the form of brass bars suspended as at (*b*) above, attention being paid to various physical properties. In table 5 the bars are arranged in order of decreasing thermal conductivity. The cross-sections of the bars were either square or circular, except in the case of Trevelyan's brass bar with the wooden handle removed.

The physical constants quoted in the table are sometimes only approximate and sometimes the mean of several values, but are sufficiently accurate for present purposes; they are in most cases taken from tables. In the case of carbon, Young's modulus was calculated after determining the density, dimensions and the vibration frequency of one of the rods.

Table 5. Bars of various materials

Material	Length (cm.)	Diameter d or thickness t (cm.)	Frequency	Duration of audibility (sec.)	Thermal conductivity	Young's modulus of elasticity (c.g.s.u. $\times 10^{11}$)	Density	Result
Copper	14·1	1·27 t	2190	16	0·9	12·3	8·9	Very loud, maintained
Aluminium	15·3	1·27 t	2290	15	0·50	7	2·6	,,
Duralumin	15·3	1·27 t	2390	30	0·31	6·9	2·8	,,
Trevelyan's brass rocker	11·2	Irregular	2420	2	0·26	10	8·4	Difficult to maintain
Zinc	14	1 d	880	2	0·26	8·7	7·1	Loud, difficult to maintain
Lead	15	1·27 d	510	0	0·08	1·6	11·4	Noise
Eureka	13·2	1·27 t	{ 3100 3260	5	0·05	16·3	8·9	Clear, difficult to maintain
,,	10·3	,,	5020	6	,,	,,	,,	,,
,,	7·1	,,	11000	3·5	,,	,,	,,	,,
Arc carbon	14·3	0·5 d	670	0·5	0·01	0·9	1·4	No sound produced
,,	18	1·2 d	820	,,	,,	,,	,,	,,
,,	19·2	1·8 d	1060	,,	,,	,,	,,	,,
,,	13·3	1·8 d	2250	,,	,,	,,	,,	,,
,,	8·2	2 d	6580	,,	,,	,,	,,	,,
Glass	30·5	1·2 d	1970	9	0·001	6	2·9	,,

It is to be noted (1) that Trevelyan's rocking brass bar with its irregular cross-section is not such a good vibrator as a simple bar. A purer note can be obtained by means of carbon dioxide than by hammering. The pureness of the notes obtained by excitation by means of carbon dioxide is an interesting feature of the phenomenon. (2) Zinc has poorer vibrating properties than brass and is accordingly difficult to maintain in vibration, though the conductivity is equal to that of brass and the note emitted is clear. (3) The pitch of the lead bar could not be determined either by hammering or by means of carbon dioxide, but considerable noise could be produced by contact with the latter. The pitch was determined in an interesting manner, namely by increasing the vibrating properties of the bar by cooling it in a vacuum flask containing solid carbon dioxide and setting it in vibration the moment it was removed. The result was in agreement with calculation. In the case of two thick lead tubes, not included in the table, it was found possible to recognize the pitches, 980 and 2400 respectively, because of the rather better vibrating properties of the tube, and to get a purer momentary note with the carbon dioxide than with the hammer. (4) Eureka was investigated on account of its particular thermal conductivity, and after the failure to produce any sound from arc carbon rods; it behaved as expected. The longest bar was not very accurately square and its vibrating properties were accordingly worse than they should be. (5) Particular attention was paid to carbon as at the time it was felt that it was the borderland substance, having regard to the thermal conductivity, between those bodies which

could and those which could not be made to vibrate. No sound has been produced in carbon. Though the damping factor is considerable, the vibrating properties of the rods are sufficiently good for a clear note to be obtained when they are hammered. In later observations, see (*i*) below, it has been shown that sound can be produced in bodies having a far smaller thermal conductivity than carbon; and in particular in a diamond. We must conclude that carbon rods, made as they are by compressing gas carbon, do not behave like such solids as metals or stones, and that the hardness of the material and not the thermal conductivity is the factor which determines that sound cannot be produced in carbon and can be produced in a diamond.

(*g*) *Tubes, rings and bells*.

(1) Large thick brass tubes. Several large brass tubes have been investigated. For example, one of them had an outer diameter of 6·3 cm., the walls were 3·5 mm. thick, the length was 10 cm., and the duration of audibility was 8 sec. The principal note which could be excited and maintained by means of carbon dioxide had a frequency of 1950 ∼. The tube was sawn into two parts one-third and two-thirds of its length respectively, and the same note was excited in each of them. The notes doubtless corresponded to flexural vibrations with the production of four nodal lines.

(2) Small thick brass tubes. Thick brass tubes have better vibrating properties than either thin tubes or solid rods. They exhibit very strikingly the fact, already noted more than once, that overtones rather than a low fundamental vibration will be excited by solid carbon dioxide. Similar results have been obtained in tubular bells.

(3) Small rings. If a wedding ring be placed on a flat surface of a carbon dioxide block, a small high note of definite pitch may be produced, lasting a few moments. This observation is recorded for two reasons. Firstly because it indicates a means of exciting vibrations in small objects which cannot conveniently be set vibrating by other means, and secondly because it demonstrates practically that it is only while the metal is losing heat to the block that the vibrations occur. The ring leaves an imprint on the block. In the case of small objects the specific heat and specific gravity are physical factors that will affect the time for which the sound will continue.

(4) Brass bells. Several hand bells have been investigated. For example, a bell that gave out sounds of frequencies 270 and 1460 with its hammer gave out the latter frequency only when excited with carbon dioxide.

(*h*) *Wires*.

(1) Sonometer. Only a very small amount of chattering can be produced in sonometer wires. We note that the mass of metal is small, and the frequencies rather low. The persistence of vibration in a particular sonometer was about a third of that of a small upright piano with the sustaining pedal down.

(2) Piano. The wires of a small upright piano were investigated with the sustaining pedal down. The unexpected result was obtained that the fundamental

tones and not the overtones are excited by the carbon dioxide down to a frequency as low as about 100 ∼. Notes of frequencies exceeding 1000 are pure, clear and maintained; as the frequencies get smaller chattering gradually increases, but it is still the fundamental that is produced and maintained. In the case of the lowest wires, corresponding to frequencies from about 30 to 180 ∼, noise, including the fundamental and the overtone three octaves above (240 to 800 ∼), was usually heard. The duration of audibility of the notes ranges from about 50 sec. for the longest, to 5 sec. for the shortest wire. Wires are the only vibrating bodies in which low frequencies have been excited; we may suppose that the difference in this respect between wires and other vibrating bodies is due to the fact that the carbon dioxide gas under pressure flows past the wire on both sides of it.

(*i*) *Miscellaneous objects.*

(1) Silver objects. As had been expected on account of its high conductivity, clear and sometimes beautiful tones can be produced in silver objects. According to Honda and Konno* the solid viscosity of silver lies between that of brass and steel. Thimbles, aural specula (about 3000 ∼) and even irregularly shaped objects can be excited so as to give out a single note. A small tea pot was made to emit a pure tone (2860 ∼) when touched at a particular place on the bottom. This picking out of a note when an object is touched at the right spot is very characteristic.

The observations made on a table spoon, dessert spoon and tea spoon respectively, touched by the blocks as indicated in table 6, are given because they emphasize the possible application of the carbon-dioxide method of excitation to picking out the resonant vibrations of irregularly shaped objects. Pure, piercing tones were sometimes obtained.

Table 6

End of handle	Between handle and centre of gravity	Near centre of gravity	On bowl
850	570	2750	Various
1150	800	4000	,,
1740	1170	—	,,

(2) Quartz. Quartz is a semi-conductor the thermal conductivity of which varies with direction. Its vibrating properties are good. The conductivity along the optic axis is 0·06 and in one direction at right angles to this it is 0·03. These values are intermediate to those of eureka and carbon respectively. Two quartz discs of diameters 5 cm. and 3·8 cm., and thicknesses 1·6 mm. and 1·8 mm. respectively were excited to give out clear notes by means of carbon dioxide, though these were not maintained. The pitch of the larger disc, determined experimentally, was 3800, while that of the smaller one, as calculated from the relative dimensions of the two, was 7400.

When a block of carbon dioxide was held against a quartz convex lens considerable noise was produced. This result was compared with that obtained with a

* *Phil. Mag.* **42**, 115 (1921).

Chladni sand figure on brass disc, produced by contact with solid carbon dioxide.
Diameter, 3 in.; thickness, 5 mm.; frequency, 2960 ~.

glass lens and a pure block of carbon dioxide ice (see § 2 below), when for the first time a very slight noise was detected with glass. It is thus just possible under the most favourable conditions, i.e. using a material with good vibrating properties and a very efficient block of carbon dioxide, to detect sound (not to produce sustained vibrations) in a material the conductivity of which is about $\frac{1}{1000}$ that of silver. Quartz is the only non-metal in which a note of definite frequency has so far been produced.

§ 2. SOME PROPERTIES OF SOLID CARBON DIOXIDE RELEVANT TO THE INVESTIGATION

It was soon noticed that the ease with which vibrations could be excited varied from day to day, and that when a fork was being excited water sometimes condensed on it near the point of contact with the carbon dioxide block. This latter fact is presumably caused by a cooling of air below the dew point. Solid carbon dioxide sublimes at about $-80°$ C.

The presence of dew led to the suspicion that changes in weather might be responsible for the differences in the results obtained on different days. However, experiments conducted (1) in a dried closed space, (2) in a moist closed space, (3) near an electric stove, and (4) in the cool atmosphere of an electric refrigerator showed that these varying external conditions produced no effect that could be appreciated, either in hindering the vibrations if these were easily excited, or in assisting their production on occasions when they were difficult to produce. In connexion with the production of ripples on mercury (see § 4 below), the question of pressure due to the weight of the block was considered; and when the density of the blocks was ascertained, by weighing and measurement, it was found to vary from day to day. This suggested the cause of the behaviour of different blocks. It is only blocks of high density which will produce sound in metals, and this doubtless is the reason why the phenomenon has not attracted more attention.

Light snow carbon dioxide, which floats on water, may be compressed into solid blocks, which vary in density and hardness according to the amount of air left in them. When sufficiently compressed they behave like ice carbon dioxide in producing vibrations, and the density of some blocks the author has handled has been as high as 1·4. It is to be noted that a block made by compressing snow may be denser at the centre than at the outside. The density of ice blocks which have been made by the process of directly freezing with the aid of liquid air also varies; an entirely solid block would have a density of 1·56, but any block consisting of solid ice crystals will be satisfactory. Some blocks contain more oil than others, and the author is inclined to consider that this reduces their efficiency in producing vibrations. Apart from actual determination of the density, it has been found possible to recognize blocks from different factories by viewing them by transmitted light, and also by rubbing a surface and watching how far a snow crust forms as sublimation occurs. Crust does not form on a good ice block.

There is some evidence of selectivity in the range of frequencies best excited by different blocks. Thus, a very efficient block excited loud notes between 2000

and 15000 ~, while a lighter and less efficient block excited the 1024 and 2000 ~ forks most easily and also excited the 1960 ~ brass bar. The production of gas-pressure is probably slower, and evidently less efficient, with blocks of low density than with those of high density.

The author is indebted to Dr Ezer Griffiths for the following data. The sub-limation temperature of carbon dioxide may vary from $-78°$ C. down to $-93°$ C. In passing from the solid to the gaseous state 1 gm. takes up 138 calories. The specific heat of solid carbon dioxide at $-78°$ C. is 0·31. The mean specific heat of the gas is 0·19. The total refrigerating effect of 1 gm. from solid to gas at $0°$ C. is 153 cal.

It is to be noted that on account of the large heat of sublimation, solid carbon dioxide can be conveniently stored for a considerable time in a vacuum flask.

§3. MISCELLANEOUS OBSERVATIONS

(*a*) *Sound produced in thermal semi-conductors.* In early observations there was no question of producing any sound from non-metal solids. We have noted however that with a pure ice block, a minute sound was detected in a glass lens.

Other non-metallic solids have accordingly been investigated. They are enu-merated below in descending order of thermal conductivity, as far as this is known, or according to the results of the carbon-dioxide test when it is unknown. Small sounds were heard when the following objects were touched with the solid carbon dioxide: various precious stones including pearls, diamonds, rubies and garnets: crystals, marble, mother of pearl, slate, glass.

No sound was obtained from wood, ebonite, paper, cork, sealing-wax, amber, ivory, or Rochelle salt. Dr Mandell kindly allowed me to try a crystal of this highly insulating, fragile material.

From these observations and from those described in the previous section we may conclude that the lower limit of thermal conductivity of a body in which it is possible to produce any sound by contact with solid carbon dioxide is about $\frac{1}{500}$ that of silver; while the lower limit for which it is possible (provided the other physical properties are suitable) to produce vibrations of regular pitch is probably about $\frac{1}{50}$ that of silver.

(*b*) *Vibrations in heated bars.* The vibrations produced in a brass bar are little affected by heating it, either by means of a bunsen flame or by means of an electric oven (in the latter case to about 180° C.). The intensity of sound which can be obtained is however reduced in a bar which is more strongly heated by means of a glass-blowing flame. The reduced effect is due to the diminishing vibrating pro-perties of the brass.

(*c*) *Liquid air.* It was not found possible to produce any sound (due to vibrations of the bar) by holding the tip of a brass bar against the surface of liquid air contained in a vacuum flask.

(*d*) *Vibrations in heated metal bars caused by contact with ice.* Clear, feeble, momentary notes, which are quenched at once by the formation of water, have actually been produced by contact with ice in heated brass bars under certain conditions. It is hoped to describe these observations when they are complete.

§ 4. EXPERIMENTS WITH MERCURY

(a) *Surface-tension ripples*. If a small block of solid carbon dioxide of high density be floated on mercury and remain stationary, it at once gives rise to ripples varying from 1 to 3 mm. in length. The frequency of the ripples may be calculated from Kelvin's formula

$$v^2 = n^2\lambda^2 = \frac{g\lambda}{2\pi} + \frac{2\pi T}{\lambda\rho},$$

where ρ and T are the density and surface tension respectively. Taking, as Vincent[*] did, values of 300 to 400 c.g.s.u. for the surface tension of mercury which has not been specially freed from grease and moisture, the frequencies are found to vary from about 100 to 500. The various effects that may be produced on the surface of mercury depend upon the size, shape and height of the floating block. Under favourable conditions many beautiful experiments may be made, such as the production of ripples, stationary ripples, interference, etc.

The under surface of the block gets worn until it has a flat polished marble-like or ice-like appearance according to whether compressed snow or ice is used; this effect can be seen if the block is looked at directly after removal from the mercury. The formation of ripples usually ceases abruptly when the height of the block has diminished to 3 or 4 mm., corresponding to a pressure due to gravity on the liquid of about $0.5 \times$ gm. wt./cm². The ripples may even cease before the height of the block has diminished to the above limit, if the under surface has had time to become quite flat. It is to be noted that there may still be a large horizontal area of contact between the block and the mercury, although the ripples have ceased.

If the block be bulky and be pressed down, commotion and bubbling of the liquid is produced; this may be compared with the noise which is made when a block makes large contact with a metal. As in the case of the production of vibrations, the change of state takes place much more rapidly while ripples are being produced.

The ripples do not cease because of the cooling of the mercury, as the bulk of this is large, and the fall of temperature, as measured by a thermometer, is small. They cease, and that suddenly, when the vertical contact is too slight, corresponding to a flat under surface and small height.

(b) *Carbon dioxide boat*. An irregularly-shaped block will give out ripples which vary in length in different directions. If it is light, i.e. not high, it will sometimes rotate and sometimes move forward. Thus a broad boat-shaped block may travel quite rapidly, if it is carved out so as to have smooth sides and a concave stern. If the dish containing the mercury be tipped so that the bottom forms as it were a shelving beach, the force with which a moving block is hurled on to the shore is obvious, and the force which must be exerted by the hand to keep it off is a valuable indication of the forces which are productive of sound when applied to massive solid metals. It seems certain that the propelling force is the pressure of the carbon dioxide gas. Visual evidence of the pressure can be obtained by watching the

[*] J. H. Vincent, *Phil. Mag.* **43**, 411 (1897).

movements of a strip of tissue paper which is held near a concavity in the block which is touching the mercury.

(*c*) *Mercury hygrometer*. If mercury be progressively cooled by contact with solid carbon dioxide, dew eventually forms on the surface. The dew forms suddenly, but owing to the ripples it appears far below the dew point. Thus on a warm damp day when the room temperature was 68° F., dew only appeared at 37° F., but then appeared copiously. On the other hand when the block was removed at the right moment leaving the surface still, dew formed at 60° F. as compared with 59° F. on the surface of a polished calorimeter containing water to which pieces of ice were added.

Thus, were it not for the ripples, mercury would offer an excellent polished surface for dew-point determinations, and solid carbon dioxide an easy method of cooling it. There might also be objections, however, from the point of view of hygrometry to the presence of carbon dioxide gas.

§5. THEORY

Gathering up the significant experimental facts, and at the same time developing a theory of the production of vibrations in solids by contact with solid carbon dioxide, we note:

(1) The source of energy is undoubtedly the heat which is transferred from the body to the carbon dioxide during momentary contacts of the two bodies. The thermal conductivity and mass of the body must be sufficient to ensure an adequate supply of heat, although the area of contact must be small. The conditions are well fulfilled with tuning forks, metal bars, thick tubes and thick metal discs, and vibrations may be maintained in these bodies for a considerable period. With the exception of the semi-conductor quartz, metals are the only materials that have been excited to give out sustained notes. Other crystals of suitable conductivity could doubtless be set in vibration. With bodies of small mass, the source of energy and consequently the vibrations cease almost immediately, because of the fall of temperature.

(2) The efficacy of solid carbon dioxide in producing vibrations is undoubtedly due to the fact that it sublimes, with the production of considerable gaseous pressures. These pressures are made evident in the experiments with mercury. The sublimation is greatly accelerated during the production of vibrations. Vibrations cannot be produced by contact of a metal with liquid air, and although under certain conditions feeble momentary notes have lately been detected when ice comes into contact with heated metals, the formation of water quenches the vibrations, and these observations confirm the view that it is the fact of sublimation that is essential to the production of loud notes. The process reminds us of the vibrations of the reed of a wind instrument. We may even speculate as to whether the contact of the gas with the metal does not produce eddies as it does in the cases of Aeolian and edge tones, and whether it would be possible to obtain magnified stroboscopic photographs by the shadow method showing how the gas is moving!

(3) The fact that the maintenance of vibrations is effected by the communication of heat makes us think of Trevelyan's rocking bar, and there are interesting similarities and differences between the two phenomena. Thus in Trevelyan's experiment it is in the body which loses heat that the vibrations are produced. Again, the production of sound depends upon the difference of temperature between the heated rocker and the block upon which it rests, and upon the sufficiently rapid conduction of heat near the points of contact.

Coming to the differences: we notice that the vibrations in the rocking bar are excited by the alternate expansions of the two portions of the lead block which come into contact with the two parallel grooves, and the resulting vibrations are mechanical or gravity vibrations of relatively low frequency, e.g. forty to several hundred*. The vibrations produced by solid carbon dioxide are elastic and of higher frequency, and as has already been stated they are caused by the impulsive pressures of the carbon dioxide as it sublimes.

(4) It is of interest that, with the exception of wires, the range of frequencies excited should be so high, for example, the overtone 3200 ∼ and not the fundamental of a 512 ∼ tuning fork will be excited by contact with solid carbon dioxide. The necessary passage of heat and sublimation must accordingly occur in an extremely short interval of time. If we try to excite too low a frequency there will be chattering because the pressure and volume of gas sublimated are so great. On the other hand it has so far been found impossible to excite frequencies above 15000. One hesitates to ascribe this to want of gas-pressure; it may be due to the inevitably small time constant of the vibrators in question, as they must either be made very thick which increases the damping factor, or very small, which diminishes the energy content, and we have seen that there is difficulty in maintaining vibrations unless the time constant is sufficient. We may well imagine that rather different conditions prevail in the case of wires and that the gas probably flows past them on both sides. Noise is obtained if the area of contact is not small. We may suppose that the metal is receiving a number of impulses from different parts of the block which do not synchronize. Once the block is worn flat the noise ceases.

(5) Finally the mechanism of maintenance may be compared to that of an ordinary electrically maintained tuning fork in which a relaxation oscillation† is excited by the vibrating body, but maintains the latter. Thus the vibrating metal determines the frequency, and the sudden gaseous pressure produced in a small cavity or groove at the point of contact of the two bodies maintains the vibrations.

A highly damped vibrator is not excited by contact with solid carbon dioxide. The author suggests that the reason why large Chladni plates as a rule only give out various noises when excited is that there are generally some four dozen possible audible modes of vibration, and that while the lower ones will not be excited, no single one among the higher modes has the necessary time constant to govern the situation and set up vibrations of one particular frequency. It is otherwise when

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* E. G. Richardson, *Phil. Mag.* 45, 976 (1923). S. Bhargava and R. N. Ghosh, *Phys. Rev.* 517 (1923).

† van der Pol, *Phil. Mag.* 51, 978 (1926).

such a plate is bowed, as the time constant is not of the same significance, and the note given out by the plate is not maintained. On the other hand it is to be expected that Chladni sand figures will be easily produced in thick metal discs with blocks of carbon dioxide.

§6. SUGGESTED APPLICATIONS AND EXPERIMENTS

In conclusion some suggestions will be made regarding possible applications of the carbon dioxide method of exciting vibrations.

(1) *Loud maintained standard frequencies.* Stout forks of frequencies ranging from 2000 to 6000 ∼, or even above this, are not easy to excite electrically, but if they are excited as described above, § 1 (*a*), loud notes may be maintained for a minute or more. These might be useful in certain wireless investigations. For some purposes an inexpensive standard would be a small thick brass tube suspended from the two nodes by threads.

(2) *Setting in vibration of metal objects* which cannot be excited by hammering, bowing or electrical methods, e.g. small rings, small bars of magnetic or non-magnetic material, or objects attached to apparatus which must not be jarred.

(3) *Recognition and accentuation of overtones.* Solid carbon dioxide may fulfil the functions of a Helmholtz resonator in a novel way, in picking out the overtones in vibrating bodies. The carbon dioxide will also maintain one overtone exclusively. This property may be of considerable value to musical instrument makers, more especially for tuning percussion instruments such as bells, tubular bells, and those instruments in which graduated metal bars are employed. The overtones of irregularly shaped bodies may similarly be excited. This may sometimes be of value to the engineer in discovering undesirable resonances in small pieces of machinery or in electric plate condensers. The damping in the case of stretched metal diaphragms is probably too great for the method to be applicable, but it would be interesting to search for resonances in these.

(4) *Rapid estimation of relative thermal conductivities in solid non-metals.* Solid carbon dioxide which has been prepared by freezing and which is free of oil may be considered to have standard properties in producing vibrations. With such a block, more or less noise may be produced by contact with solid substances which are semi-conductors, as for example quartz, marble and other stones, and it is only in substances with high insulating properties such as sealing-wax, ebonite, amber or cork that no sound whatsoever can be detected. These facts may be of interest to the geologist. Again quartz lenses can be immediately distinguished from glass lenses by bringing them into contact with solid carbon dioxide.

(5) *Setting in vibration of piezo-electric crystals of audible frequency**. No experi-

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* Since the above was written a natural quartz crystal, $5\frac{1}{2}$ in. long and of cross-section about $\frac{1}{2}$ in., has been tried at the Natural History Museum. A loud maintained note was produced, of frequency just above 4000 ∼. The note is harder to start than in the case of metals, because of the smaller thermal conductivity; on the other hand the loudness increases very rapidly. A crystal, $2\frac{1}{2}$ in. long and of cross-section about $\frac{1}{4}$ in., has been investigated in the laboratory, the frequency in this case being about 6000 ∼. It is hoped shortly to try a bar of square cross-section which is being cut from a large crystal.

mental work has been done on this subject, but in a crystal such as quartz which has considerable thermal conductivity one would expect interesting results since it was found possible to produce a note in a quartz disc. The method has been found useless in the case of crystals of low thermal conductivity, such as Rochelle salt.

(6) *Study of ripples in mercury* (see § 4 above).

(7) *Mercury hygrometer* (see § 4 above).

DISCUSSION

Mr G. G. BLAKE asked whether the wave-length of the ripples produced on mercury was related to the size of the piece of carbon dioxide employed. He had found that when solid carbon dioxide was allowed to form bubbles in a liquid, the speed of bubbling increased as the size of the solid was diminished, and depended also on the nature of the liquid, large bubbles being produced at a slow rate in thick oil.

Principal S. SKINNER said that the phenomenon described was analogous to the spheroidal state of water.

Mr C. R. DARLING suggested that graphite might behave similarly to metals towards solid carbon dioxide. He thought that the traditional explanation of the singing kettle needed revision, because a glass beaker did not give the same result as a copper kettle. The conductivity of the material had to be taken into account.

Mr R. APPLEYARD suggested, in the light of an experiment by Prof. Boys, that the mercury ripples might be due to breakdown of the surface tension of the mercury. It was possible to project a demonstration of the spheroidal state optically by running a drop of water down a vertical platinum wire on to a hot plate, and projecting the end of the wire; it would be interesting if the author could project one of her experiments in a somewhat similar way. Had the phenomenon anything to do with cavitation? Was the surface of the metal roughened?

Mr F. C. MEAD suggested that the failure of carbon to vibrate might be due to its absorbing the gas.

Dr J. E. R. CONSTABLE: The author mentioned that the period of decay of her vibrating bars when struck depended but slightly upon the weight of the hammer used for the striking. I would suggest that this can be simply explained by the logarithmic nature of the decay of the oscillations, and does not need the hypothesis of variation of internal viscosity with amplitude which was advanced. Judging from the intensity of the sound generated by the bars exhibited by Miss Waller I should say that the initial amplitude is probably about 10^4 times the final amplitude and, since the time of decay of the sound is proportional to the logarithm of the initial amplitude, a factor of 2 or 3 in this amplitude will produce only a comparatively small change in the decay period.

Prof. A. O. RANKINE said that the last speaker's suggestion was borne out by Dr A. H. Davis's experience in using a tuning fork as a standard of comparison in noise-measurement. Small variations in the initial amplitude of the fork did not seriously impair the consistency of the results.

AUTHOR'S reply. In reply to Mr Blake: Factors which increase the gas-pressure between the block of carbon dioxide and the mercury diminish the wave-length of the ripples produced. Thus a higher block (within limits) or a concavity at the side of the block near the surface of the mercury diminishes the wave-length. See also § 4 of the paper.

In reply to Principal Skinner: The minimum difference between the temperature of the metal plate and the boiling point of water necessary to produce the spheroidal state is about 40° C. This is of the same order of minimum temperature-difference as that which must exist between metal and carbon dioxide if vibrations are to be produced. For example, a brass bar, cooled by means of solid carbon dioxide, gave no sound when touched with carbon dioxide until its temperature had risen from − 80° C. to about − 30° C. A practical difficulty in getting very exact results arises from the fact that hoar-frost forms on the metal.

I am much obliged to Mr Darling for very kindly sending me a specimen of Acheson graphite. Noise is produced when it is brought into contact with solid carbon dioxide; moreover the frequencies of vibration of several bars have been recognized. The notes cannot be maintained for any considerable period. The thermal conductivity of graphite is much greater than that of carbon, and its apparent density is 1·56 while its real density is 2·21; hence its porosity is 28 per cent, which is less than that of carbon.

In further reply to Mr Darling and in reply to Mr Mead: I find that notes can be produced and maintained for a few seconds in a carbon rod on which copper has been deposited electrically. Mr G. E. H. Rawlins suggested this experiment. It would seem that the porosity is the determining factor in preventing the production of vibrations in carbon rods.

In reply to Mr Appleyard: An attempt to project a demonstration in an optical lantern was not successful. I have not found that metals are in any way physically affected by the gas-pressure of the carbon dioxide.

I agree that the constancy of the results obtained by hand-hammering is sufficiently accounted for by the logarithmic nature of the decay of the vibrations, as suggested by Dr Constable. In experiments with brass bars of the same frequency, 2070 ∿, but of different masses, and hammers of 120 and 5 gm. weight respectively, I find that with bars whose masses are greater than about 100 gm., the heavier hammer, while with bars less than 100 gm. in mass, the lighter hammer, is the more efficacious. With bars of about 100 gm. it matters little which hammer is employed. The fact that hand and ear can give such consistent figures is of considerable interest.

A SENSITIVITY-CONTROL FOR THE LINDEMANN ELECTROMETER

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ABSTRACT. A circuit is given for varying the sensitivity of the Lindemann electrometer by means of one adjustment only.

THE following method of controlling the Lindemann electrometer, originally designed for the benefit of unskilled operators in connexion with an instrument recently described in these *Proceedings**, will commend itself to users of this type of electrometer on account of its simplicity and convenience. It allows the sensitivity to be varied continuously over a wide range by means of one adjustment only, without the zero being thereby disturbed.

The sensitivity of the Lindemann electrometer is a function of the total voltage between the quadrants, which are charged to opposite potentials of approximately equal magnitudes, the departure from exact equality being occasioned by a lack of symmetry in the mechanical construction, which makes it necessary to apply a slightly greater voltage-difference to one pair of quadrants than to the other in order that the electrical zero may coincide with the mechanical zero. If the voltages required on the two pairs of quadrants for balance at different sensitivities be measured, it will be found that they are always in a constant ratio. A typical set of results is given in the table below, the last column of which shows that, for the particular instrument on which these measurements were made, the quadrant potentials for balance must be in the ratio 1·06 : 1, at all sensitivities.

Quadrant potential relations at balance for a Lindemann electrometer.

Sensitivity (divisions per volt)	Total voltage $(V_A + V_B)$ between quadrants	Voltage V_A on negative quadrants A	Voltage V_B on positive quadrants B	V_B/V_A
9·0	34·6	16·8	17·8	1·06
17·5	49·0	23·8	25·2	1·07
34·0	58·2	28·2	30·0	1·06
73·5	65·0	31·7	33·3	1·05
120	68·2	33·2	35·0	1·05

This fact permits the use of the circuit shown in the diagram. Two fixed and two variable resistances are placed in series with a dry battery of from 70 to 80 V. The quadrants A and B of the electrometer are connected through safety resistances,

* *Proc. Phys. Soc.* **44**, 445 (1932).

of 2 MΩ each to the ends of the fixed resistances, and the earthed case of the electrometer is connected to the moving arm of the variable resistance R_1. The latter is adjusted, once for all, so that the potentials V_A and V_B, applied to the quadrants A and B respectively, are in the correct ratio required for balance. The potentials V_A and V_B may then be simultaneously varied by altering the value of the series resistance R_2, whilst the ratio V_B/V_A remains constant, so that the sensitivity can be varied whilst the zero remains undisturbed.
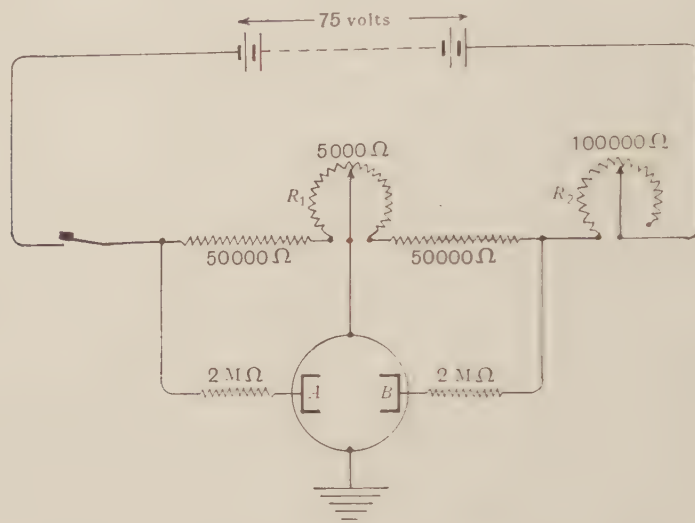
Circuit for controlling sensitivity of Lindemann electrometer.

Resistances of high values, totalling 250,000 Ω or more, should be employed in order that the current drawn from the dry cell may not exceed a fraction of a milliampere. Such resistances can readily be obtained as standard radio components.

If desired, another variable resistance of lower value may be placed in series with R_2 to serve as a fine adjustment. The advantages of this system are that it is compact, and that it dispenses with secondary cells and tedious double adjustment.

DISCUSSION

Mr F. J. SCRASE. The arrangement described is likely to prove useful when the Lindemann electrometer is used at high sensitivities. If, however, only moderate sensitivities are required it is unnecessary to maintain such a precise balance of the voltages on the two quadrants. At Kew Observatory, in using Lindemann electrometers at a sensitivity of about 40 divisions per volt for atmospheric electrical measurements*, we find that 16½-volt grid-bias batteries with tappings at 1½-volt intervals provide sufficiently fine adjustment of the plate potentials to keep the electrical zero within a few divisions of the mechanical zero. This entirely obviates

* *J. Sci. Inst.* **9**, 246 (1932).

the necessity for using balancing resistances, and the sensitivity can be varied in convenient stages by simply moving the two tapping plugs. Moreover, any particular sensitivity of the series available can be repeated readily and accurately, the fall in sensitivity due to deterioration of the batteries being less than 1 per cent per month, whereas if a variable resistance is used it is necessary either to calibrate the electrometer after every readjustment or to have the resistance graduated so that it can be reset accurately in any desired position.

AUTHOR'S reply. I am obliged to Mr F. J. Scrase for his interesting note. I would like to point out, however, that the arrangement he describes permits only of a discontinuous variation of sensitivity by a series of jumps corresponding to the several battery tappings, whereas the method described in the paper was designed expressly to give a continuous variation of sensitivity together with an unvarying zero, so that any desired value of the sensitivity could be instantly obtained. We are using the Lindemann electrometer in conjunction with a high resistance to form a delicate galvanometer for the direct measurement of the ionization currents from small γ-ray sources, and require to be able so to adjust the electrometer sensitivity that the steady deflection of the needle corresponds numerically to the strength of our radium sub-standard. This can only be achieved by a method which provides a very fine control of sensitivity, and a great deal of time is saved if the zero remains unchanged during the process of variation. A fixed zero has the further advantage, in a direct-reading instrument of this kind, that the observed deflection can be read straight off on the eye-piece scale, without the necessity of applying a zero correction.

It was arranged that the electrical zero should coincide with the mechanical zero at all sensitivities, not so much from a desire to preserve a precise electrical balance throughout (although, of course, this is important at high sensitivities) as because it was the only way of keeping the zero constant. With regard to calibration, I personally would always prefer, except for the roughest kind of measurements, to calibrate the electrometer before and after a series of readings, rather than to trust to the constancy of batteries or of resistance settings.

No doubt Mr Scrase finds his arrangement entirely suitable for his own work, where apparently a displacement of the zero does not matter and where a close control of sensitivity is not wanted, but I feel that the circuit which I have given is of more general application and covers the whole range of usefulness of the Linde-mann electrometer in a perfectly satisfactory manner.

KINEMATIC SUPPORTS AND CLAMPS

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Lecture delivered November 4, 1932.

As this society takes all physics to be its province, it may be willing to turn aside for a few moments from the main stream of progress in order to revisit the little backwater in which important principles of instrument-design were originally expounded, and to enquire whether these principles cannot be invoked even on behalf of the clamp, an appliance which, unlike its more aristocratic sister-in-law the support, has hitherto been the unskilled and unconsidered drudge of the laboratory and the workshop.

Let us, in the first place, define the precise sense in which we propose to use these two names.

It is well known that an unconstrained rigid body has six degrees of freedom in relation to its surroundings, that to constrain a surface of the body to touch a given surface fixed relatively to the surroundings reduces the number of degrees of freedom by unity, and consequently that if six suitably chosen surfaces must be touched no freedom remains and the body is definitely fixed. These six surfaces may be said to form for the rigid body a *kinematic support with zero degrees of freedom*.

It is, perhaps, not so generally recognized to be characteristic of this system that the supporting surfaces will not by their joint actions exercise any forces upon the supported body in the absence of some agent additional to them, such as gravity or the pressure of a spring. If such an agent is present it is manifestly distinct from the six fixed supporting surfaces and is in no danger of being confused with any one of them.

If, however, such an agent is absent, or is to be disregarded, and a seventh surface suitably placed relatively to the other six is moved up to the rigid body so as to exert a pressure P upon it, the other six surfaces will now exert pressures each equal to P multiplied by a factor which is constant for that surface. These seven surfaces may be described as forming a *kinematic clamp with zero degrees of freedom*, and this is illustrated by the model shown in plan and side-view in figure 1. The model consists of a triangular base-board carrying three V-shaped brackets through which pass three pairs of adjustable screws with rounded ends, which by themselves would serve as a kinematic support for the three-rayed body with prismatic lower surfaces which is indicated by the dotted lines. The base-board also carries another bracket through which passes a seventh screw which can touch the supported body at its centre of gravity G. It might be imagined that this seventh screw could not be considered as comparable with the other six, but merely as a reinforcement of

gravity, but if the base-board is turned over so as to face downwards and any one of the seven screws is slackened it will be seen that the supported body will still rest against the seventh screw and any five of the other six, which in this case are to be considered as together forming the kinematic support from which the clamp is evolved, this evolution being effected by the subsequent tightening of any one of the seven screws.
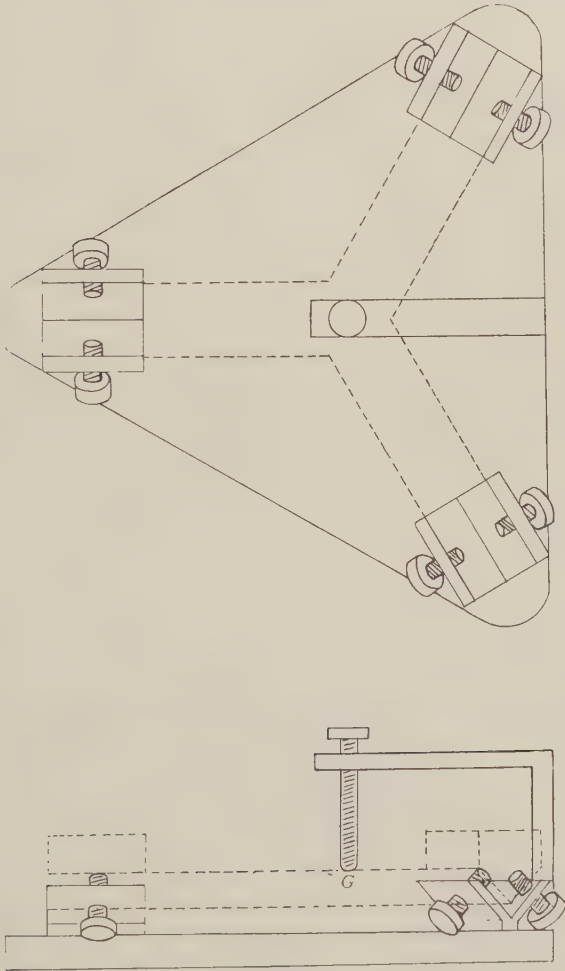
Figure 1.

The behaviour of this model thus illustrates the general statement that in a kinematic clamp with zero degrees of freedom all its seven surfaces must be con-·sidered as contributing to it on absolutely equal terms, because any six of them could be taken as constituting a complete kinematic *support* in which pressures were produced by the presence of the seventh.

It is seen to be a characteristic feature of a kinematic clamp that, while the pressures exerted by its surfaces are indeterminate, depending upon what we may

call the tightness of the screwing up, they will bear determinate and constant ratios to each other.

If we now pass to the case of a rigid body which is required to have a single degree of freedom, the condition to be imposed is that it should touch five suitably chosen surfaces. We may describe these surfaces as forming a *kinematic support with one degree of freedom*. The free motion will be unresisted except by friction, but, as before, in the absence of an external agency the supporting surfaces will not of themselves exert any pressure on the supported body.

If a sixth surface is now moved up to the rigid body, so as to touch it at a point A, the six surfaces will ordinarily form a kinematic *support* with zero degrees of freedom as previously defined, and a screwing up of the sixth surface will lead to motion of the body according to the freedom defined by the other five, but not to the production of continued pressures by any of the surfaces.

If, however, the freedom defined by the five surfaces is such that the initial direction of motion of the point A is tangential to the sixth surface, or alternatively that it has no initial motion, a screwing up of the sixth surface will not lead to any motion of the rigid body, but to the production of pressures by all the surfaces, whose absolute magnitudes will depend upon the tightness of the screwing, but whose ratios will be determinate and constant.

This, as we have seen, is the characteristic property of a kinematic clamp, and it is appropriate therefore to call such a system a *kinematic clamp with one degree of freedom*, the free motion being resisted by friction only.

As before, all the six surfaces involved may be considered as contributing to the clamp on absolutely equal terms.

In general, the system of surfaces will only behave as a clamp for a definite position of the rigid body, and the possible free motion must be treated as only a small displacement from that position, while a finite displacement would either be resisted by jamming or would involve loss of contact with one of the surfaces; but in particular cases the possible range of motion may be finite.

These statements may be illustrated by the behaviour of a simple model in which part of the lower surface of the rigid body is prismatic and another part is a plane parallel to the edge of the prism. The rigid body has attached to its upper surface (1) a glass plate not parallel to the edge of the prism, (2) another glass plate parallel to this edge, (3) a small convex lens, (4) a small concave lens, the tangent plane at the middle of either lens being parallel to the edge of the prism.

Of the five surfaces which form the kinematic support, two touch one of the surfaces of the prism, two the other surface of the prism, and one the remaining plane lower surface; thus every point of the rigid body is free to move in a straight line parallel to the edge of the prism. A sixth surface, the end of a screw carried by a bracket, is now moved up to the rigid body so as to press it towards the other five, and to touch it at a point A which by adjustment of the bracket may be made to lie on any of the surfaces (1) to (4).

If the surface (1) is selected, the line of movement of A is not parallel to the tangent plane at A; screwing up the sixth surface will continuously displace the

rigid body and the six surfaces will form a kinematic support with zero degrees of freedom. If the surfaces (2), (3) or (4) are selected, and if, in the latter two, A is at the middle of the lens, the line of movement of A is parallel to the tangent plane at A; screwing up the sixth surface will not displace the rigid body but will produce pressures on all the surfaces, and the system will be a kinematic clamp with one degree of freedom. In this case, if the curvature of the surface of the rigid body at A is such that the line of movement of A lies inside the body as with surface (4), the free motion could not be of finite range on account of jamming. If it lies outside the body, as with surface (3), the free motion if of finite range would involve loss of contact with the sixth surface, but if a finite length of it lies along the surface of the body, as with surface (2), the free motion will have a possible range equal to this length, during which the system will continue to act as a clamp.

A different assemblage of surfaces may be employed as a further illustration of these principles. In this form of model three planes approximately perpendicular to each other and intersecting at a point A are set up facing three similar planes intersecting at a point B, in such a position that all the planes make nearly equal angles with the line AB. If a body of suitable dimensions is placed between them it can be turned until it touches all the planes. In order to maintain these contacts some external agent having a moment about the axis AB must be applied to the body; the system will then be a kinematic support with no degrees of freedom, and in the absence of such an external agent no pressures will be produced by combined actions of the supporting surfaces consequent on a change in the distance AB. If, however, this distance is increased to the maximum value consistent with the existence of the six contacts, the planes will, if pressed together, exercise pressures upon the enclosed body when no external agent is applied to it, and the system will become a kinematic clamp with one degree of freedom but infinitesimal range, a finite rotation producing cessation of contact.

Similarly if the distance AB is decreased to the minimum value allowed by the presence of the enclosed body and the planes are pressed together, the body assumes a definite position without any need for the application to it of any external agent, the planes exercise pressures upon it, and the system again becomes a kinematic clamp with one degree of freedom but infinitesimal range, a finite rotation being resisted by jamming.

Finally, if the enclosed body is bounded by a surface of revolution, the system will in no case be a kinematic support, and when the distance AB is diminished until the six contacts are made it becomes a kinematic clamp with one degree of freedom and unlimited range.

The full consideration which we have given to the case of a single degree of freedom enables us to traverse more rapidly the wider field opened to us when the postulated number of degrees of freedom is increased. It is readily seen that in each case a kinematic clamp can be evolved from the appropriate kinematic support by a transition similar to that which has already been studied, namely that an additional surface must be provided, and that this surface must touch the supported body at a point A, such that each one of the hitherto possible free motions of the

body will either leave the point A initially at rest or produce an initial movement of A in the tangent plane to the surface of the body at A. For example, if two points A and B are taken on the surface of the rigid body such that the tangent planes at A and B are each perpendicular to the line AB, then if two surfaces are made to touch the body at A and at B respectively they will constitute a kinematic clamp with five degrees of freedom, a very inefficient form of constraint, but one into which a badly designed boss-head often degenerates.

The principles which we have enunciated will find practical application in the design of clamps for holding various pieces of apparatus. When the position of such apparatus is required to be adjustable, it is essential that the possible degrees of freedom, which are governed partly by the geometrical shape of the apparatus and partly by the disposition of the clamping surfaces, should at least provide for all the desired movements of adjustment. The process of tightening, while producing the friction necessary to maintain the apparatus in position, will not tend to disturb the adjustments.

When the shape of the body which is to be clamped is given, some general considerations as to the appropriate form of clamp are at once evident. If the
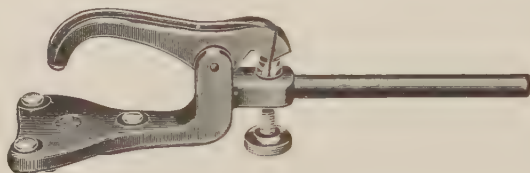
Figure 2.

body is a sphere it is obvious that its three degrees of rotational freedom cannot be interfered with except by friction, and therefore a four-surface clamp will be appropriate. If the surfaces of the body available to the clamp are two parallel planes, the same reasoning and result hold good, and the pattern, illustrated in figure 2, gives effect to these considerations.

If the clamp is to be applied to the surface of a circular cylinder, one degree of rotational freedom and one of translational freedom must remain, and a five-surface clamp will be needed. Convenient forms of boss-head and clamp embodying this design have already been described*. Two of these are shown in figures 3 and 4.

Finally, if the body to be clamped is a surface of revolution, since one degree of rotational freedom must remain, the clamp must have six surfaces.

If the body is prolate, the system of two rectangular corners already demonstrated could of course be employed to furnish the six surfaces required. If, on the other hand, the body is oblate, and particularly if it is lenticular, a convenient pattern of clamp consists of two V grooves meeting at an obtuse angle and forming four of the surfaces, the other two being supplied by a third V groove cut in a suitably curved pressure-arm, adjustable by means of a screw and link. It has been proved (*loc. cit.*) that the required curve is the involute of a circle, if the clamp

* *J. Sci. Inst.* **7**, 119 (1930).

is to be available for discs of widely differing diameters. This clamp is shown in figure 5.

When clamping surfaces are applied to spheres, parallel planes, circular cylinders, or surfaces of revolution the range of the motions corresponding to the various degrees of freedom will be unlimited except by the dimensions of the clamped body, and no possibility of either jamming or loss of contact will exist.
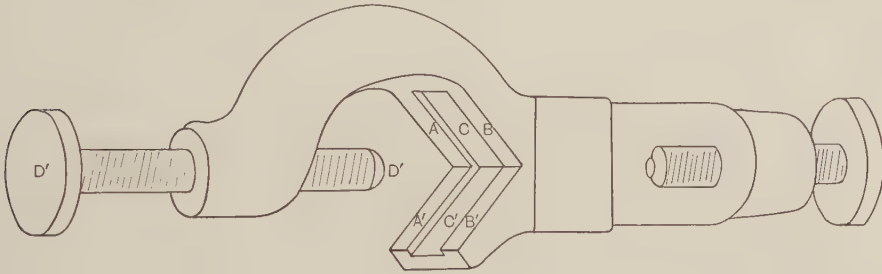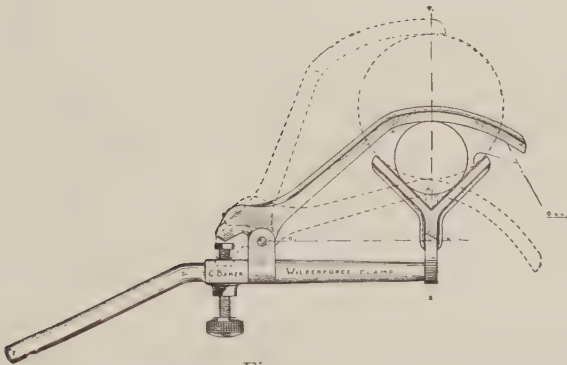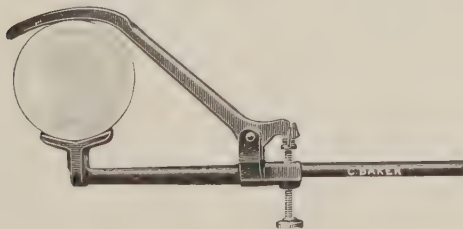
Figure 3.

Figure 4.

Figure 5.

In conclusion, it should be pointed out that the practical forms of clamp which have been exhibited have no claim to be called kinematic except when they are engaged upon the surfaces for which they are designed. The five-surface cylinder-clamp, for example, is no longer kinematic when applied to a cone. Indeed, it is clear that no kinematic clamp can be designed for a conical surface, if limited to it. It is true that a cylinder-clamp can be used for holding a retort by its rapidly tapering neck, and is a convenient device for the purpose, but it accomplishes this feat only by an illegitimate appeal to friction, successful in the event, but completely alien from its better nature, as I have tried to expound the latter in this lecture.

REVIEWS OF BOOKS

The structure of molecules, edited by P. DEBYE. Authorized translation by W. M. DEANS, M.A., B.Sc. Pp. vii + 190. (London: Blackie and Son, Ltd.) 15s.

The problem of molecular structure is one which has long occupied the attention of chemists, and, in the case of the compounds of carbon in particular, a large amount of accurate information is available as to the relative positions of atoms and groups in molecules, and the particular types of valency linking between them. This information is hardly likely to be seriously modified by the application of physical methods. The interatomic distances and the possibility of freedom of rotation about valency bonds are also in most cases qualitatively known from investigations in stereochemistry. In recent years considerable interest has been shown in the bearings of chemical structure on physical properties, and *vice versa*; and by the use of information derived from investigations of dipole moments and spectra, for example, considerable progress has been made in refining the conceptions already known to chemists and, in many cases, in providing numerical values for the interatomic distances and the relative strengths of valency bonds. This is more particularly true in the region of very simple molecules; in the case of polyatomic molecules progress, as Prof. Mecke points out in the present book, is more difficult, although there seems reason to hope that much will be done in this field in the future.

The papers deal with free rotation in organic molecules, the analysis of band spectra of polyatomic molecules, the bearings of the Raman effect on molecular structure, dissociation, predissociation, and problems of valency. Each is contributed by a recognized expert and the collection is useful, although so much advanced mathematics and knowledge of spectrum notation is assumed that it is to be feared that the organic chemist, who is contributing most of the material on the chemical side, may find much of it practically unintelligible.   J. R. P.

Recent advances in atomic physics, by Prof. GAETANO CASTELFRANCHI. Translated by Dr W. S. STILES and Dr J. W. T. WALSH. Vol. 1: Atoms, molecules and electrons. Pp. xii + 360 with 111 illustrations. Vol. 2: Quantum theory. Pp. xii + 400 with 79 illustrations. (London: J. and A. Churchill.) 15s. each.

Unlike Prof. Newman's companion volume on "non-atomic" physics, this work is addressed more to the general reader than to the student of physics. It will, however—on the whole deservedly—almost certainly enjoy a large circulation among readers of the latter class.

The book will give to the average reader a very fair, though necessarily superficial, view of recent work in atomic physics. It also deals briefly with much of the earlier work from which the new advances have most directly derived. The historical perspective thus offered should be of special value to the young student of physics, though it is avowedly incomplete, and occasionally inaccurate in detail. There are excellent bibliographies, and the author's selection of references is pleasingly international—although it is more than a little surprising to find no reference to Rayleigh in the account of thin oil films.

The whole treatment is of necessity highly compressed, but the exposition is very lucid, and the topics are well selected and arranged. Young readers should be warned of the presence of errors, of which some, but not all, are obvious at sight; there is one very distressing definition—"*the unit quantity of X-rays is that which produces in one cubic centimetre of air under normal conditions one electrostatic unit of electricity.*"

Minor criticisms apart, Prof. Castelfranchi is to be complimented upon his success in compressing a remarkable survey of modern atomics into a very readable and handy book.

The translators have done their work competently, especially with the less ornate passages of the original text, and they have performed a real service in making the book more accessible to English readers.   H. R. R.

Electrical phenomena in gases, by K. K. DARROW. Pp. xvii + 492. London: Baillière, Tindall and Cox. 42s. net.

Dr Darrow's book differs considerably in plan and style from existing treatises of similar scope, to which, therefore, it forms an acceptable supplement. With it, and with the completion of the revised edition of the first great English classic on conduction in gases, English readers will again possess a really adequate introduction to the latest developments in this important and difficult field of physical inquiry.

The book may be divided into two sections, roughly equal in length. The first and slightly longer of these contains a connected and acutely critical account of the elementary processes occurring in excited and ionized gases. There are full discussions of the genesis and "recombination" of ions, of the properties of positive and negative ions, as deduced from their motions amidst—and through—neutral gas molecules under varied pressure conditions and with and without electric fields, and of cognate topics.

This first section therefore contains those portions of the subject which can profitably be discussed on straightforward theoretical lines, with a reasonable minimum of un-verifiable assumptions. The second section (chapters IX to XIII) deals with more complex and highly important gaseous-discharge phenomena which are not as yet susceptible to precise quantitative treatment. The scope can best be indicated by citation of chapter head-ings: IX. Self-amplified ionization (Townsend's "ionization by collision") and breakdown; X. Space-charge; XI. Plasma and sounding-electrodes; XII. The self-sustaining glow; XIII. The self-sustaining arc.

The treatment is everywhere as clear as the difficulties of the subject permit—Dr Darrow makes full use of his well-known gifts for both popular and technical exposition. In discussing experimental work, he concentrates on the principles of an experiment (mainly with a view to the unambiguous interpretation of the resulting measurements) rather than on details of experimental technique. A beginner in the subject, or a reader with no more than a general interest in it, and a disinclination to spend much time in consulting original papers, would probably appreciate a more lavish display of tables of numerical data than is granted to him in this book—but this is not a very serious criticism. Some border-line topics—for example, cathodic sputtering—are wholly or partially omitted, but it must be assumed that these omissions are deliberate. On the whole, the treatment is very well balanced, and the book makes a notable addition to the literature of electricity in gases.

The book is well produced, and the price—considering the present exchange—not disproportionately high.   H. R. R.

Tables of cubic crystal structure, by I. E. KNAGGS, Ph.D., B. KARLIK, Ph.D. and C. F. ELAM, M.A., D.Sc. Pp. 90 + blank pages for notes. (London: Adam Hilger, Ltd.) 11s. 6d.

The object of this book is to provide a handy volume of reference to the published data on crystals having a cubic structure.

The book is divided into two parts. The first part, which deals with elements and compounds, has been compiled by Drs Knaggs and Karlik, whilst the second part, which

deals with alloys, is due to Dr Elam. Each part consists of two tables and a bibliography. In the first table the substances are arranged alphabetically and in the second they are arranged in order of spacing. The first table gives references to the bibliography, and the index number of each substance in the second table. The latter gives the lattice-size and the type of lattice on which the structure is based. Chemical composition, description of phase (in the case of alloys), and general remarks are also included in the tables. Although obvious to anyone familiar with the work, it might perhaps have been made clear that the lattice (simple, face-centred, or body-centred) associated in the tables with each substance is really the type of lattice on which the structure is based, and not the structure of the substance itself.

Details of structures cannot, of course, be obtained from the book; it has not been written for that purpose. Its usefulness lies rather in its conciseness, which makes it possible to see at a glance how much work has been done on a particular substance and where a description of that work may be found. The list of references is complete up to August, 1931.

Such a book as the one under review must inevitably become out of date fairly rapidly, and we are pleased to see that the authors intend to revise the tables and bring them up to date from time to time. May we hope that the authors will also extend their work to structures other than cubic. By doing so they would compile a valuable store of information.

<div align="right">J. T.</div>

A textbook of physics, by E. Grimsehl. Translated from the Seventh German edition by L. A. Woodward, B.A. Vol. 1: Mechanics. Pp. xii + 433 with numerous figures, appendix, tables, examples and answers to examples. (London: Blackie and Son, Ltd.) 15s. net.

The subject of elementary mechanics has always been the sport of mathematics, physics and engineering departments, the difficulty being that whereas the mathematician has little patience for experimental verification, the physicist, and still more the engineer, does not require analytical rigidity. We are so surrounded by mechanical devices that we are apt to forget that the mechanical principles involved are very few indeed and very simple, so that a teacher may easily in these days fall into the error of overstressing the example rather than the principle underlying it. This is the tendency in the present book, which purports to be of the "standard of a degree in physics." The reviewer thinks that the standard ranges from pre- to post-intermediate and could be read equally well by physics and engineering students. This does not detract from the interest of the book provided it gets into the right hands. The subject matter is far too diffuse to detail here; it ranges from the parallelogram of forces, Archimedes' principle and pulley systems to vortex motion, space lattices and aeroplanes. It is encyclopaedic in its outlook. The student of physics would be far better advised to use the book for extending the applications of the principles of mechanics that he has already acquired a knowledge of. The derivation of Poiseuille's formula is inserted as an afterthought in small print at the end of the book, whilst as an offset against this almost a full page is occupied by a *picture* of an analytical balance and half a page with the "rotor or runner of a Francis turbine," whatever that may be. In the tables the density of wax is 0·96. What is wax? The elastic constants are expressed in tons per square inch.

The book could be read with great interest by the young engineer-physicist, but the exposition of the principles of mechanics for degree students in physics should be a much more formal undertaking.

<div align="right">L. S.</div>

Intermediate physics, by C. J. Smith, Ph.D., M.Sc., A.R.C.S. Pp. viii + 650 with illustrations and diagrams. (London: E. Arnold and Co.) 14s.

The tail must continue to follow the head, and Dr Smith's text-book is an excellent example of this truth. Any good teacher or examiner possesses intuition of the standard of knowledge that can be expected from a given group of pupils. The assessment of this standard must be made in relation to the current and ever increasing knowledge of the subject.

About 108 pages are devoted to properties of matter, 130 to heat, 150 to optics, 50 to acoustics and 200 to electricity and magnetism. In the first section such subjects as diffusion, high vacua, surface tension, viscosity and elasticity are dealt with. Even though there is nothing in the index to indicate that viscosity has been considered, yet in the text the standard methods for determining viscosity are described. However laudable it is to introduce in its own place an illustration of a petrol pump as a harmless example of a suction pump, it is to be doubted if a description of the cup-and-ball viscometer will add anything to an intermediate student's knowledge of the principles of physics. The section on heat is enriched with many new diagrams that have not appeared before in an elementary text book. The student is given the advantage of first-hand knowledge of the standard work on the subject of the late Prof. Callendar. The optical section is illustrated with a set of exceptionally clear diagrams. The treatment of geometrical optics is concise. Perhaps a little attention might have been given to colour-vision, and the direction of the light across the retina in figure 288 should be marked. In this section the introduction of the wave theory, the diffraction grating and the sagittal method are merely signs of changing times. The section on acoustics is comparatively ordinary; this is more surprising in view of the remarkable developments that have taken place in this science in recent years.

An excellent treatment of the subject of magnetism with a fine set of diagrams is marred a little by the absence of arrows indicating the direction of the lines of force. It is pleasing to see that in the treatment of the magnetic effects of a current circuit the so-called law of Biot and Savart is subordinated to the far more general and valuable idea of the equivalence of a current circuit and a magnetic shell. It is to be hoped that all the rules for the mutual effect of magnetic fields and currents will eventually disappear except the right-hand-screw convention. They are bad physics. The useful convention distinguishing inductive from non-inductive winding seems to have been dropped in this part of the book. The electron makes its appearance at the end of this section and even the Planck-Einstein photoelectric equation is introduced.

The work is excellently produced. It is a pleasing book to handle and strikes the teacher immediately as being the work of an author with a wide and balanced outlook on an ever changing subject.

L. S.

Physical principles of mechanics and acoustics, by R. W. Pohl. Translated by Winifred M. Deans. Pp. xii + 338. (London: Blackie and Son, Ltd.) 17s. 6d.

A man is seated on a stool, of which the seat is free to rotate without friction, and holds in his right hand a vertical or nearly vertical shaft to the upper end of which is attached a wheel, with its spokes perpendicular to the shaft, free to rotate about the shaft as an axle. The whole arrangement is thus somewhat similar to an umbrella upheld in use. Now, with the left hand, he sets the wheel revolving. What will happen?

For a second problem, the man is again seated on the stool, but an assistant has the umbrella. He sets the wheel revolving, and hands the umbrella to the seated man. Is the result the same as before?

These problems are typical of those dealt with in this book, which is very truly a physical introduction to mechanics, since its outlook is entirely experimental though not

elementary. In comparison with it almost all other books on the subject are mathematical books. The author, since he appeals only to principles and to experiment, has no objection to the discussion of subjects which the orthodox text-books of hydrodynamics would class as too difficult for treatment—and this without using an integral sign in the whole course of the work.

With a book of such an original outlook, it would be impossible in a review to draw attention to all the novelties. It must suffice to give a few examples, and to say that whilst all physicists (particularly those who teach mechanics) ought to read it, any engineer who does so will be almost certain to benefit by it. Mathematicians, too, might well read it, for they would thereby acquire a humble spirit. They would see a new classification of what is elementary and what is advanced, and there is every possibility that they might be stimulated to treat theoretically (though approximately) problems which are here treated experimentally.

The book opens unconventionally, with a discussion of length, time, velocity and acceleration measurements; the notion of time is reduced to that of uniform rotation, and, to fix ideas, the velocity of a rifle bullet is determined by the method of letting it pierce two rotating discs in succession. For the acceleration due to gravity, Atwood's machine is dispensed with and the actual acceleration of a falling body is directly measured; time is again reduced to uniform rotation, this time with a rotating jet of ink. The student cannot fail to see that what is being measured is the acceleration g, and he can verify that it is independent of the material of the falling body. The next subject is the philosophically difficult one of force, mass and Newton's laws; again the treatment is original and sound. After a chapter on simple harmonic motion and central orbits, the subject of weight and attractions is taken up, and then the concepts of work, energy and momentum are introduced and discussed. The chapter on rotation of rigid bodies is a fascinating one. It includes the gyrostat, with the phenomena of nutation and precession, and picks its examples from such diverse matters as a reel of thread dropped on the floor, the methods of Chinese rope dancers, the rotation of the ordinary electric fan, the " clear circle " which the gymnast carries out on the horizontal bar, riding a bicycle with the hands off the handle-bars, and many another. The method of observing an instantaneous axis is worthy of special mention. On a rotating body, paste a piece of newspaper: the print is completely blurred except at the intersection with the instantaneous axis. What could be simpler?

One longs for space to dilate on the next chapter, entitled "Accelerated systems of reference." It again is experimental, and it is the chapter from which the reviewer believes he has learnt most.

The last two chapters of the mechanics section deal with hydrostatics and hydrodynamics. Since the treatment is experimental, viscosity and turbulence are treated as fully as the more elementary part of the subject. The treatment shows that the author is fully cognizant of modern work on eddy formation and cognate matters.

The acoustics section is as refreshing as the mechanics part. A chapter on vibrations includes treatments of resonance, Fourier analysis, forced and coupled vibrations, amplification and rectification. Its examples are taken from vibrations of all kinds. It is followed by a chapter on waves and radiation, which is of interest far outside the narrow range of acoustics. Most of the experimental waves are water waves produced in a ripple tank. By setting up slits of diminishing sizes, the author demonstrates first rectilinear propagation, then diffraction into the edge of the shadow, and finally, passing to a very small slit, he shows this acting as a source. This gives an experimental basis for Huyghens' principle, and then by remembering that phase must be taken into account, the ordinary Fresnel-Huyghens theory is developed. It is used in the customary way to account for interference, diffraction, reflection and refraction, each checked experimentally. By using a Galton whistle, with its very short wave-length, sound can be manipulated almost as easily as light, especially when the sound radiometer is used as detector. Even the

interferometer is dealt with in this chapter, and Bragg's law for reflection of radiation by a space lattice finds a place.

In the body of this review several types of people were recommended to read the book, and the omission of the student from this list was intentional. He would undoubtedly learn a great deal if he stopped to perform the experiments, but few students would feel that they had time for this. Moreover, despite the fact that his grasp of fundamentals would almost certainly be exceptional, he would not be in a position to satisfy the examiners. To reach this point, he would have to practise the numerical application of principles to specific (often trivial) examples. In this respect the book under review does nothing for the student. It is true that it contains at the end a collection of sixty examples for the student to work at, but they are all very elementary and, in any case, one example for each five pages of text is too few.

Attention is drawn in the publisher's announcement, and in the preface, to the figures. Many of these are silhouettes, and they do not seem to the present reviewer to have the advantages claimed for them. The book is beautifully printed and produced, and the thirteen plates contain figures to which nothing but praise can be given.   J. H. A.

The history of the microscope, by R. S. CLAY, B.A., D.Sc., F.Inst.P. and THOMAS H. COURT. Pp. xiv + 266. (London: C. Griffin and Co., Ltd.) 30s.

Historical studies have an inimitable fascination for folk with the necessary degrees of imagination, patience, and leisure; but the full fruitfulness of such researches cannot be experienced till we have penetrated behind the crumbling stones, the rusted arms and the decaying finery, the superficial noise of battles and wrangle of politics, to the minds and hearts of human beings grappling with the difficulties of their day. History is not of uniform value, and the past leaves but few straws on the tide of forgetfulness, but there are curiosities still to be rescued and arranged, lovingly tended and admired. Not everybody will find this book appeal to him, and indeed its meticulous attention to the details of the instruments it describes will only be fully appreciated by the fortunate few who have managed to become the possessors of at least a small collection of old microscopes, or whose enthusiasm is unchastened by the glass of museum cases.

The story stops short at the period of the introduction of the achromatic microscope and, much as we may appreciate the thoroughness of the work, it is the reviewer's opinion that a single volume embracing the whole development of the instrument from ancient times to the present day would have been far more useful to the vast majority of readers, of whom comparatively few will be museum curators, or even collectors. The authors hope, however, to prepare a further volume in which the history will be continued.

It goes without saying that this book affords a very thorough survey of the early mechanical evolution of the microscope. The early models designed by Hooke, the fine adjustment of Hevelius, the improvements due to Culpeper, Cuff, Benjamin Martin and many other famous makers, both British and Continental, are brought before us in a succession of beautifully printed and illustrated pages, so that we can admire the simplicity and directness of design of the Italian models illustrated on page 80, deplore the unnecessary scrolls and flourishes of the Chérubin instrument shown on page 81, and wonder at many other similar contrasts.

The book is not without its touches of whimsical fun, as when it calls attention to the influence of candlestick design on the form of some of the compound microscopes of the eighteenth century.

Many facts, not usually known, in connexion with the optical evolution of the instrument are brought to light; for instance, the claim of Monconys to be the originator of the use of a field lens added to a Keplerian eyepiece to increase the field of view. On the optical side, however, the authors are not so happy, and do not always effectively help

the reader to distinguish between the true and the false steps of the early makers; there is a slip for example in referring to the supposed correction for spherical aberration effected between the eye and field lens of an eyepiece, whereas chromatic aberration of magnification is the real correction. These, however, are matters of detail. In its main purpose, which is to bring us into understanding of the patient trials of our predecessors in this field, and at the same time to furnish an authoritative book of reference, the book succeeds extraordinarily well. No reference library can afford to be without it, and true lovers of old instruments will find it a treasure-house of delight.   L. C. M.

Atmospheric electricity, by B. F. J. SCHONLAND. Pp. 100 with 25 diagrams. (Methuen's Monographs on physical subjects, London, 1932.) 2s. 6d. net.

This excellent little book gives a concise and interesting account of atmospheric electricity as this term is generally understood; that is to say, it is concerned with the electrical properties of the lowermost layers of the atmosphere, up to about 15 km. It has four chapters, devoted respectively to the ionization of the (lower) atmosphere, the penetrating radiation, electric fields and currents in the atmosphere, and the electrification of thunderstorms. The book forms a valuable introduction to this important subject.

                                                                        S. C.

The equivalent temperature of a room and its measurement. Building Research Technical Paper No. 13, by A. F. DUFTON, M.A., D.I.C. Pp. v + 9. (London: H.M. Stationery Office.) 6d.

The rate of loss of heat from the human body in a room may depend not only on the temperature, movement, and humidity of the air, but also on the temperatures of the various surfaces in the room. Comfort may not be entirely determined by the rate of heat-loss, but a step forward is made by setting up a definite method of comparing rooms in respect of their influence on this loss. It is proposed to do this by stating an equivalent temperature characteristic of any room. This is the "temperature of a uniform enclosure in which, in still air, a sizable black body at 75° F. would lose heat at the same rate as in the environment." The report discusses this method and describes an instrument for determining the equivalent temperature so defined, which is not the same as the "effective temperature" used in America. The latter attempts to assess the comfort, rather than merely to measure a heat-loss.   J. H. A.

Induction coil theory and applications, by E. TAYLOR JONES, D.Sc. Pp. viii + 244 with 131 illustrations. (London: Pitman and Sons, 1932.) 12s. 6d.

When Prof. Taylor Jones began his investigations on the induction coil our knowledge of the theory of the action of this important piece of apparatus was decidedly incomplete, and the elements of its design were consequently somewhat rule-of-thumb. He has for the first time cleared up the subject, and by his exhaustive experimental work not only verified his theory but added materially to our knowledge of the behaviour of the induction coil. In order to cope with the problems presented on the experimental side he has invented two instruments, an electrostatic oscillograph and a current oscillograph. A full account of all this, accompanied by many oscillographic records, is to be found in the present volume.

A chief feature of the induction-coil discharge is seen, in the light of the author's work, to be the fact that it is oscillatory, and that in virtue of the magnetic coupling between the primary and the secondary there is a double oscillation in each of these circuits. The work described relates to the ordinary induction coil with make and break in the primary, to the Tesla coil and the auto-transformer, and to the high-tension magneto. The discharge through X-ray tubes, of the gas and Coolidge types, and the

question of the most effective adjustment of a coil for the production of X-rays, are treated at some length.

To a large extent the present book is a revised edition of the author's previous work entitled *The theory of the induction coil*, published eleven years ago. There are in addition three entirely new chapters. One is devoted to the study of spark ignition, and an examination of the thermal and electrical theories of ignition. A second chapter is devoted to experiments on the oscillations in the magnetically coupled circuits of a triode thermionic valve. The third contains an account of the author's interesting research on the diffraction of electrons, preceded by an exposition of the foundations of electron wave theory and of the experimental work of Davisson and of G. P. Thomson.

The appearance of this book will be warmly welcomed and appreciated equally by the physicist and by the electrical and the automobile engineer. D. O.

Mathematical tables, Vol. **3**, by THE COMMISSION FOR THE CONSTITUTION OF THE STARS OF THE INTERNATIONAL ASTRONOMICAL UNION AND THE BRITISH ASSOCIATION COMMITTEE FOR THE CALCULATION OF MATHEMATICAL TABLES. Pp. viii + 34. (London: Office of the British Association.) 10s.

Volume 1 of the B.A. mathematical tables contained a variety of functions of general utility, and a promise to complete the collection by publication of the various Bessel functions tabulated in the course of the life of the B.A. Committee. This promise has not yet been redeemed. Instead, we have the somewhat specialized Emden functions, which, in the present state of stellar dynamics, can fairly be said to be of topical interest. They are the solutions of the differential equation $x d^2y/dx^2 + 2dy/dx + xy^n = 0$ which represents the equilibrium of a mass of gravitating gas obeying the polytropic condition $p = \kappa\rho^\gamma$ where p and ρ are pressure and density respectively and $\gamma = (1 + 1/n)$. When n is less than 5 the mass of gas has a boundary, but not otherwise. The state of a sphere of gas at uniform temperature is a limiting case as n tends to infinity.

For $n = 5$, the equation happens to be soluble, y being the algebraic function $(1 + x^2/3)^{-\frac{1}{2}}$. Again, when n is unity, $y = \sin x/x$ and when $n = 0$, the general solution is $A + B/x - x^2/6$, or (with the boundary conditions required for the present problem), $y = 1 - x^2/6$. This particular case has naturally no astronomical application. Emden, in a book published in 1907, gave tables of the solution of the differential equation for a number of values of n, including the limiting case as $n \to \infty$ when the equation becomes

$$x d^2y/dx^2 + 2dy/dx + xe^y = 0.$$

The present volume contains tables of y to seven figures for $n = 1, 1\cdot5, 2, 2\cdot5, 3, 3\cdot5, 4$ and $4\cdot5$, each with sufficient derivatives to enable interpolation to be carried out by Taylor's theorem, to the full seven figures. To assist in this, a table of $h^r/r!$ (the coefficient of the derivative in Taylor's series) is given in an auxiliary table, p. 32. It covers $h = 0$ to 1 by steps of $0\cdot01$, and $r = 1$ to 6 inclusive and should be useful to users of tables other than these. In addition to the tables of y and its derivatives, certain other related functions of y and x are tabulated, except in the case of $n = 1$. They are placed in comfortable proximity to the main function itself. For interpolation in these tables, Lagrange's formula is recommended, and the necessary tables to apply this method easily are given at the back of the volume.

For the limiting case $n = 5$, when y is algebraic, only five figures of its value are given, and the auxiliary functions are omitted.

The tables seem to be conveniently arranged in every way and only the astronomical user can say whether it is a serious defect that they disregard the fact that y is a function of two arguments, n and x. Everything is done to facilitate interpolation for x, but no indication is given as to how to proceed if a solution is required for, say, $n = 2\cdot85$ instead of one of the round values tabulated. J. H. A.